TKK Reports in Forest Products Technology, Series A10
Espoo 2009

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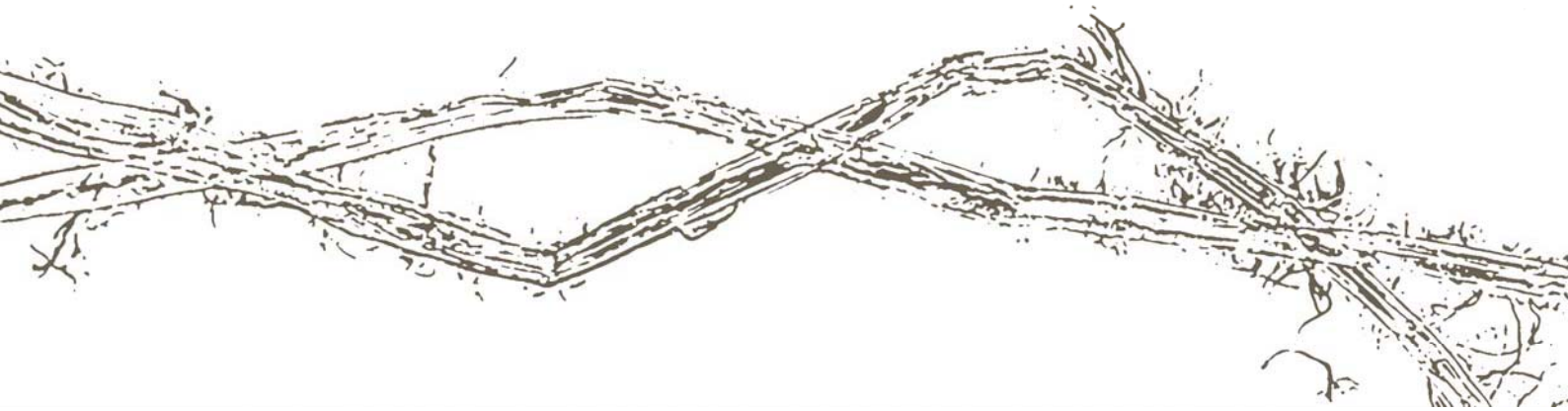
Doctoral Thesis

Petri Myllytie



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Petri Myllytie

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Faculty of Chemistry and Materials Sciences for public examination and debate in Auditorium Puu II at Helsinki University of Technology (Espoo, Finland) on the 18th of December, 2009, at 12 noon.

Helsinki University of Technology
Faculty of Chemistry and Materials Sciences
Department of Forest Products Technology

Teknillinen korkeakoulu
Kemian ja materiaalitieteiden tiedekunta
Puunjalostustekniikan laitos

ABSTRACT OF DOCTORAL DISSERTATION	HELSINKI UNIVERSITY OF TECHNOLOGY P.O. BOX 1000, FI-02015 TKK http://www.tkk.fi

Author Petri Myllytie

Name of the dissertation
Interactions of polymers with fibrillar structure of cellulose fibres: A new approach to bonding and strength in paper

Manuscript submitted September 17, 2009	Manuscript revised November 16, 2009
Date of the defence December 18, 2009	
☐ Monograph	☒ Article dissertation (summary + original articles)

Faculty	Faculty of Chemistry and Materials Sciences
Department	Department of Forest Products Technology
Field of research	Forest Products Chemistry
Opponent(s)	Professor Robert Pelton
Supervisor	Professor Janne Laine
Instructor	Ph.D. Susanna Holappa

Abstract

The interactions between paper strength enhancing polymers and cellulose fibrils were studied at molecular and microscopic levels with cellulose model surfaces and with fibril and fibre suspensions. Paper sheet experiments were performed to evaluate the influence of different polymers at macroscopic level on the development of bonding and strength in paper. The main objectives of the work were: 1) to further the understanding on the development of tensile properties of paper from a wet sheet to a dry paper and on the mechanisms of action of different strength additives 2) to resolve the specific interactions of certain polymers with cellulose and 3) to relate the molecular and microscopic level phenomena to the development of bonding and strength in paper.

Adsorption of polymers was highly dependent on the interactions between cellulose and the polymers as well as on the adsorption conditions. The dispersing or aggregating effects of polymers on cellulose fibrils were observed at molecular and microscopic levels in model systems and on the surfaces of cellulose fibres. The adsorption of polymers also affected hydration and viscoelastic properties of the fibril/polymer layer. Polymer adsorption, when carefully considered, can provide an easy control over stabilization, compatibilization, and water affinity of fibrillar cellulosic materials.

The development of tensile properties of paper upon drying was characteristic for each polymer and adsorption condition. The increased dispersion and plasticization of cellulose fibrils on fibre surfaces by carboxymethyl cellulose and xyloglucan influenced the development of fibre bonding and paper strength during drying. In addition, the development of drying tension showed differences between polymers, thus it could be possible to utilize additive-specific drying conditions to attain the desired end properties of a paper product.

The ability of chitosan to act as a wet web strength additive in paper was related to the pH dependent adsorption behaviour of the polymer. Chitosan was found to adsorb on cellulose in the absence of electrostatic attraction, demonstrating the specific interaction between the polymers. The wet web strength improvement was partly attributed to increased wet adhesion between chitosan coated cellulose surfaces at high pH but covalent bonding was likely to impart the wet web strength as well.

Keywords	Paper strength, polymer adsorption, strength development, fibre bonding, strength additives		
ISBN (printed)	978-952-248-228-0	ISSN (printed)	1797-4496
ISBN (pdf)	978-952-248-229-7	ISSN (pdf)	1797-5093
Language	English	Number of pages	81 p. + app. 84 p.
Publisher	Helsinki University of Technology, Department of Forest Products Technology		
Print distribution	Helsinki University of Technology, Department of Forest Products Technology		
☒ The dissertation can be read at http://lib.tkk.fi/Diss/2009/isbn9789522482297			

VÄITÖSKIRJAN TIIVISTELMÄ	TEKNILLINEN KORKEAKOULU PL 1000, 02015 TKK http://www.tkk.fi

Tekijä Petri Myllytie

Väitöskirjan nimi
Polymeerien ja selluloosakuidun fibrillirakenteen väliset vuorovaikutukset: Uusi lähestymistapa kuitujen sitoutumiseen ja paperin lujuuteen

Käsikirjoituksen päivämäärä 17.9.2009	Korjatun käsikirjoituksen päivämäärä 16.11.2009

Väitöstilaisuuden ajankohta 18.12.2009

☐ Monografia	☒ Yhdistelmäväitöskirja (yhteenveto + erillisartikkelit)

Tiedekunta	Kemian ja materiaalitieteiden tiedekunta
Laitos	Puunjalostustekniikan laitos
Tutkimusala	Puunjalostuksen kemia
Vastaväittäjä(t)	Professori Robert Pelton
Työn valvoja	Professori Janne Laine
Työn ohjaaja	FT Susanna Holappa

Tiivistelmä

Paperin lujuutta parantavien polymeerien ja selluloosafibrillien välisiä vuorovaikutuksia tutkittiin molekyyli- ja mikrotasoilla selluloosamallipintojen sekä fibrilli- ja kuitususpensioiden avulla. Polymeerien vaikutusta selluloosakuitujen sitoutumiseen ja paperin lujuusominaisuuksien kehittymiseen tutkittiin arkkikokeiden avulla. Työn tavoitteina olivat: 1) ymmärtää miten paperin lujuusominaisuudet kehittyvät kuivatuksen aikana ja millä tavoin eri lujuuslisäaineet vaikuttavat, 2) selvittää polymeerien ja selluloosan välisiä spesifisiä vuorovaikutuksia ja 3) yhdistää molekyyli- ja mikrotason ilmiöitä kuitujen sitoutumiseen ja paperin lujuuden kehittymiseen.

Polymeerien ja selluloosan väliset vuorovaikutukset ja valitut olosuhteet vaikuttivat voimakkaasti polymeerien adsorptioon selluloosafibrillien pinnalle. Selluloosafibrillien dispergoituminen tai aggregoituminen polymeerien adsorption vaikutuksesta havaittiin sekä mallimateriaaleilla että selluloosakuitujen pinnalla. Polymeerien adsorptio vaikutti myös veden sitoutumiseen fibrilleihin ja siten systeemin viskoelastisiin ominaisuuksiin. Polymeerien adsorptiolla voidaan säätää eri sovelluksissa tärkeitä ominaisuuksia kuten fibrillisuspension stabiilisuutta, kompatibiliteettia ja veden sitoutumista.

Paperin lujuusominaisuuksien kehittyminen kuivatuksen aikana oli tunnusomaista eri polymeereillä ja adsorptio-olosuhteilla. Karboksimetyyliselluloosan ja ksyloglukaanin adsorption aiheuttama kuitujen pintafibrilleiden dispergointi ja plastisointi vaikuttivat kuitujen sitoutumiseen ja paperin lujuuden kehittymiseen kuivatuksen aikana. Polymeerit vaikuttivat eri tavoin myös kuivatusjännityksen kehittymiseen, mikä voisi mahdollistaa kuivatusolosuhteiden optimoinnin polymeerin ja haluttujen tuoteominaisuuksien perusteella.

Kitosaanin erityinen kyky parantaa sekä märän että kuivan paperin lujuutta liittyi polymeerin pH-riippuvaiseen adsorptioon ja faasikäyttäytymiseen. Kitosaanin ja selluloosan välinen spesifinen vuorovaikutus havaittiin, kun kitosaani adsorboitui pysyvästi selluloosamallipinnalle ilman elektrostaattisen attraktion vaikutusta. Märän paperin lujuuden parantuminen korkeassa pH:ssa adsorboidun kitosaanin ansiosta yhdistettiin selluloosapintojen välisen adheesion kasvuun kitosaanin läsnä ollessa, mutta myös kovalenttinen sitoutuminen on todennäköisesti yksi kitosaanin vaikutusmekanismeista.

Asiasanat Paperin lujuus, polymeerien adsorptio, lujuuden kehittyminen, kuidun sitoutuminen, lujuuslisäaineet

ISBN (painettu) 978-952-248-228-0	ISSN (painettu) 1797-4496
ISBN (pdf) 978-952-248-229-7	ISSN (pdf) 1797-5093
Kieli Englanti	Sivumäärä 81 s. + liit. 84 s.

Julkaisija Teknillinen korkeakoulu, Puunjalostustekniikan laitos

Painetun väitöskirjan jakelu Teknillinen korkeakoulu, Puunjalostustekniikan laitos

☒ Luettavissa verkossa osoitteessa http://lib.tkk.fi/Diss/2009/isbn9789522482297

PREFACE

This study was carried out in the Department of Forest Products Technology at Helsinki University of Technology during 2004-2009. The financiers of the research, National Agency for Technology and Innovation (TEKES) along with industrial research parties, Kemira Oyj, M-Real, and UPM, are gratefully acknowledged for their contribution.

I am grateful to my supervisor Professor Janne Laine for giving me the opportunity to work in the Research Group of Forest Products Surface Chemistry, and secondly, for giving me the freedom towards the scientific objectives of the study and the responsibilities for the projects under which the work was conducted. My advisor, Dr. Susanna Holappa, is gratefully acknowledged for her dedication, especially during the last steps of this thesis. My co-authors, Jouni Paltakari, Jihui Yin, Lennart Salmén, and Jani Salmi, are thanked for their involvement and insight to the research.

All my past and present colleagues, friends, and personnel at the former Laboratory of Forest Products Chemistry are thanked for the kind, helpful, and inspiring working environment. Aila Rahkola, Marja Kärkkäinen, and Ritva Kivelä are thanked for their invaluable help in the laboratory work. Librarian Kati Mäenpää is acknowledged for her help with the numerous literature acquisitions and Laboratory Engineer Riitta Hynynen is thanked for helping with all practicalities. As a member of the "Joyful Coffee Group" I would like to thank everyone involved, especially Tuula, Susanna, Katri, and Juha as an integral part of my intellectual welfare. I have had the privilege to be able to attend several international conferences, to meet new colleagues, and to see some unforgettable places during my work. My fellow scientists, Tekla, Miro, Eero, and Tuomas, just to name a few, are appreciated for all the science and fun on the road.

Foremost, my heartfelt thanks are to my family and friends for their support.

Espoo, November 16th, 2009

Petri Myllytie

LIST OF PUBLICATIONS

This thesis is mainly based on the results presented in five publications which are referred as Roman numerals in the text. Some additional published and unpublished data is also related to the work.

Paper I Myllytie, P., Holappa, S., Paltakari, J. & Laine, J. (2009). Effect of polymers on aggregation of cellulose fibrils and its implication on strength development in wet paper web. *Nordic Pulp & Paper Research Journal* 24, 125-134.

Paper II Ahola, S., Myllytie, P., Österberg, M., Teerinen, T. & Laine, J. (2008). Effect of polymer adsorption on cellulose nanofibril water binding capacity and aggregation. *BioResources* 3, 1315-1328.

Paper III Myllytie, P., Yin, J., Holappa, S. & Laine, J. (2009). The effect of different polysaccharides on the development of paper strength during drying. *Nordic Pulp & Paper Research Journal*, accepted.

Paper IV Myllytie, P., Salmén, L., Haimi, E. & Laine, J. (2009). Viscoelasticity and water plasticization of polymer-cellulose composite films and paper sheets. *Cellulose* DOI: 10.1007/s10570-009-9376-z.

Paper V Myllytie, P., Salmi, J. & Laine, J. (2009). The influence of pH on the adsorption and interaction of chitosan with cellulose. *BioResources* 4 1647-1662.

Author's contribution to the appended joint publications:

I, III-V Petri Myllytie was responsible for the experimental design, performed the main part of the experimental work, analysed the corresponding results, and wrote the manuscript.

II Petri Myllytie participated in defining the research plan with the co-authors, performed the confocal laser scanning microscopy experiments, and wrote the corresponding parts in the manuscript.

LIST OF ABBREVIATIONS

AFM	atomic force microscopy
AGU	anhydroglucose unit
CLSM	confocal laser scanning microscope
CMC	carboxymethyl cellulose
C-PAM	cationic poly(acrylamide)
cryo-SEM	cryogenic scanning electron microscope
CS	cationic starch
D.S.	degree of substitution
DMA	dynamic mechanical analysis
IR	infra-red
LS	Langmuir-Schaefer
MF	melamine-formaldehyde
MFC	cellulose microfibrils
$NaHCO_3$	sodium bicarbonate
NFC	nanofibrillar cellulose
PAE	poly(amideamine) epichlorohydrin
PDADMAC	poly(diallyldimethylammonium chloride)
PEI	poly(ethylene imine)
PVAm	polyvinylamine
QCM-D	quartz crystal microbalance with dissipation
R.H.	relative humidity
SEM	scanning electron microscope
SPR	surface plasmon resonance
TEA	tensile energy absorption
TEM	transmission electron microscope
TG	thermogravimetry
UF	urea-formaldehyde

TABLE OF CONTENTS

1 INTRODUCTION, AIMS, AND OUTLINE OF THE STUDY

The mechanical properties of paper are of prime importance in regard to paper manufacturing and the end-uses of paper products as well as in paper recycling. Almost as long as man has made paper, first by hand and then industrially, different additives have been applied in order to improve the mechanical properties of paper. The development of papermaking additives and the accumulation of practical experience of their use, combined with profound understanding of their action mechanisms, along with modern process design, have helped to realise the present state-of-the-art paper production lines. Recently, paper production has been constrained by energy and raw material costs as well as overproduction in some segments. Hence, there is a constant drive towards the use of more inexpensive raw materials and towards reduction in the basis weight of paper products while aiming to maintain the critical product properties at acceptable levels. Strength properties of paper products have been considered as the crucial properties that have limited the use of low-cost raw materials beyond conventional levels. Therefore, a fundamental understanding of paper strength by basic research is necessary to generate innovative solutions, whether new chemical additives, novel process design, or optimization of existing methods in paper manufacture.

Traditionally, paper strength additives have been divided by purpose into dry and wet strength additives (Chan 1994; Reynolds 1980). Naturally, the influence of these additives on paper properties, their use in different processes (paper grades), and their action mechanisms have been widely studied for a long time (Espy 1995; Hubbe 2006; Lindström et al. 2005). However, the fundamental understanding of paper as a material still lacks a consistent view of the underlying mechanisms of paper strength development and of the function of different strength additives.

Most strength additives are polymers – synthetic, natural, or chemically modified natural polymers – and, since they are mixed with pulp suspensions, their interactions with the pulp components in water are of vital importance when considering their effect on paper strength. Due to the heterogeneity of real paper stocks and the interdependence of adsorption, retention, and formation, the interactions of polymers

with different pulp components are complicated and the true effect of an additive is easily masked. Therefore, well-defined model systems with a reduced number of variables are required to resolve the interactions and to further contribute to the understanding of paper as a material.

In this thesis a new outlook to fibre bonding and paper strength was adopted in order to explain the interactions between strength additives and fibres and to understand the mechanisms of development of strength and the influence of the polymers applied. This way of thinking emerged from the recent studies on fibre fine structure (Duchesne & Daniel 1999), theoretical considerations of fibre surface structure in water (Pelton 1993), fibre bonding (Hubbe 2006; Torgnysdotter 2006), and the development of cellulose model surfaces (Kontturi et al. 2006). The idea is to consider the wet fibre surface as a gel-like layer consisting of hydrated cellulose microfibrils (incl. hemicelluloses). When polymeric additives are adsorbed onto the fibres, they are mixed with the fibrillar gel-like layer and will change the properties of the layer depending on the interactions between the fibrils and the polymers. On consolidation, these fibril-polymer layers form fibre bonding domains and upon drying, the interactions between the cellulose fibrils and the polymers will affect the development of the fibre-fibre bonds. Hence, the molecular level interactions between the cellulose fibrils and the additives will also essentially affect the wet web strength, strength development during drying, and the final properties of dry paper. In general, the outlook described above can be thought of as a bottom-up approach from molecular level interactions to microscopic and macroscopic phenomena in paper, and to the properties of paper as a material.

In this thesis of basic research, an approach derived primarily from adsorption, adhesion, and polymer sciences was applied to study the fibre bonding and paper strength, and the mechanisms of action of different paper strength additives. The main objectives were the following: first, to further the understanding of mechanical behaviour of paper in respect to development of strength upon drying and to the mechanisms of action of different strength additives; second, to resolve the specific interactions of certain polymers with cellulose; and third, to relate the molecular level phenomena to the development of paper strength and final sheet properties.

An introduction to the adapted approach to fibre bonding, along with microscopic and macroscopic observations on the interactions between cellulose fibrils and polymers, are presented in **Paper I**. The ability of polymers to influence the inherent aggregation tendency of cellulose microfibrils in a model system and on fibrillated fibre surfaces was studied by microscopic methods. Composite materials prepared from cellulose fibrils and polymers were mechanically tested in order to evaluate the interactions between components and the behaviour of the fibre bonding domain. A measurement set-up for evaluating the development of sheet tensile strength during drying was introduced. The characteristic effect of polymers on strength development was demonstrated.

The microscopically observed interactions between cellulose fibrils and polymers were further studied on a molecular level by adsorption experiments of different types of polymers on cellulose nanofibril model surfaces in **Paper II**. A Quartz crystal microbalance with dissipation (QCM-D) device provided information on the adsorption behaviour of the polymers, on the viscoelastic properties of the fibril/polymer layer, and on the influence of polymers on the hydration of the nanofibril layer. The QCM-D measurements were complemented by surface plasmon resonance (SPR) adsorption experiments. In addition, the interactions in aggregated cellulose nanofibril suspensions were evaluated by confocal scanning laser microscopy (CLSM). The study (Paper II) was a joint publication as a part of recent comprehensive research into cellulose nanofibrils (Ahola 2008).

Certain polysaccharides are known to have specific interactions with cellulose and have been used and studied as strength additives in papermaking. In **Paper III**, the effects of cationic starch, guar gum, xyloglucan, chitosan, and carboxymethyl cellulose on the development of sheet tensile properties and drying tension were studied with the method introduced in Paper I. The simplified model system, which was designed to emphasize the interactions between fibrillated fibre surfaces and polymers, helped to distinguish the effects of polymers on the rheological behaviour of paper. The specific interactions between the polysaccharides and the cellulose fibrils on the fibre surfaces influenced both the adsorption and the development of bonding and tensile properties during drying. The development of tensile properties proved to be very characteristic for each polymer and different adsorption conditions.

As a part of Paper I, composites of cellulose microfibrils (MFC) and polymers were tested in order to model the mechanical behaviour of the fibre bonding domain. Thus far the experimental data had indicated that plasticization by water was essential in regard to tensile properties of polysaccharide materials. **Paper IV** focused on the plasticizing effect of water on MFC-polymer composite films and paper sheets. The viscoelastic properties of composite films and paper sheets were studied with dynamic mechanical analysis (DMA) as a function of relative humidity (R.H.). The moisture affinity of the composite films was measured by thermogravimetry (TG). In addition, scanning electron microscopy (SEM) was used to evaluate the effect of polymers on the structure of the composite films.

The peculiar adsorption behaviour and superior wet web strength and strength development obtained by chitosan (Papers I and III) justified the further examination of the molecular level interactions between cellulose and chitosan in **Paper V**. Adsorption of chitosan on a cellulose model surface and the viscoelastic properties of the cellulose/chitosan layer were monitored by QCM-D at different pH conditions. The atomic force microscopy (AFM) colloidal probe technique was used to measure the surface forces between cellulose surfaces in the absence and in the presence of adsorbed chitosan at different pH conditions. Special attention was paid to demonstrate the proposed specific non-electrostatic interactions between the polymers and to elucidate the function of chitosan as a paper strength additive.

2 BACKGROUND

2.1 Cellulose fibre structure

Cellulose is the most common organic polymer on earth, produced by biosynthesis in annuals and perennials in enormous quantities. The primary molecular structure of cellulose is simple, but its ability for inter- and intramolecular interactions, the formation of several levels of organization, and its unique pathways of biosynthesis in nature have constantly motivated interdisciplinary research on cellulose.

Cellulose is a linear homopolysaccharide that consists of repeating anhydroglucose units (AGUs), more precisely, β-(1-4)-D-glucopyranosyl units, as shown in Figure 1. Depending on its origin, one cellulose molecule can contain up to 15000 anhydroglucose units, commonly expressed as the degree of polymerization (DP). Cellulose molecules in papermaking pulp fibres typically have a DP of 500-2000 depending on the wood source and the pulping and bleaching processes (Gullichsen & Paulapuro 2000). The large number of hydroxyl (-OH) groups on the cellulose chain (three groups per AGU) provides an extensive intra- and intermolecular network of hydrogen bonding, which essentially affects the structural hierarchy and the properties of cellulose.

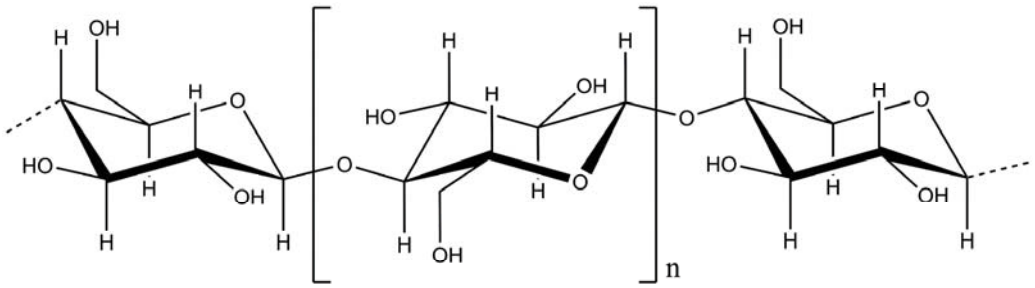

Figure 1. *Structure of cellulose.*

Cellulose is a semicrystalline polymer and its crystallinity depends on the origin and on the isolation and processing methods. The complex structural hierarchy of cellulose, due to profuse hydrogen bonding, is manifested by the existence of several

polymorphs (crystalline forms). The crystalline forms of cellulose I_α and I_β exist in native cellulose at different ratios that depend on the origin of the cellulosic material. Less organized (amorphous) cellulose is also present along with the crystalline cellulose. The crystalline forms I_α and I_β differ by their crystalline unit cell structure and overall hydrogen bonding pattern, but the main intermolecular hydrogen bond is the same for both, i.e. O6-H → O3 (Figure 2). The intramolecular hydrogen bond of O3-H → O5, which is partly responsible for the cellulose chain stiffness and contributes to load transfer along the chain, is also indicated in Fig. 2. Other crystalline forms of cellulose include cellulose II, cellulose III, and cellulose IV, that are not native forms of cellulose but formed upon chemical processing. Cellulose III and IV are mainly of scientific interest, but cellulose II is of technical relevance because it is formed in the mercerization and the regeneration processes of cellulose. Cellulose II differs from cellulose I by O6-H → O2 intermolecular hydrogen bonding and by antiparallel chain orientation (Dumitriu 2005; Hofstetter et al. 2006; Nishiyama et al. 2002; Nishiyama et al. 2003).

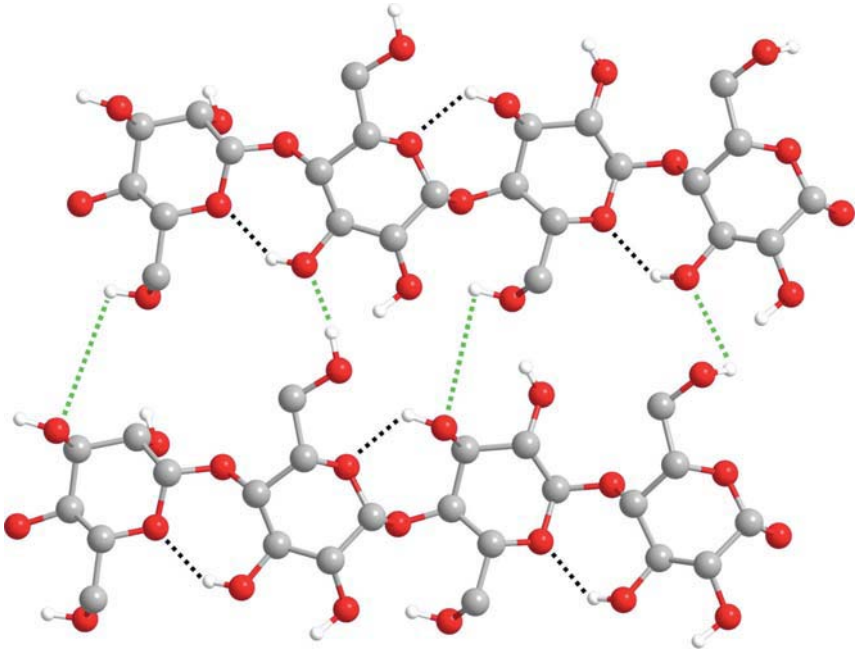

Figure 2. *Supramolecular structure of the cellulose I polymorph showing the main intermolecular O6-H → O3 (green) and intramolecular O3-H → O5 (black) hydrogen bonding patterns (a simplified schematic).*

In higher plant cell walls, the dominant structural features are layered networks of cellulose fibrils. An elementary fibril consist of 36 hydrogen bonded cellulose chains produced by cellulose synthases during biosynthesis in growing cells (Ding &

Himmel 2006; Jarvis 2003; Somerville et al. 2004; Sticklen 2008). The fibrils are further associated into larger aggregates (nano- and microfibrils) which then, together with other cell wall polymers (hemicelluloses, pectin, lignin), form the layered cell wall structure of wood fibres (Figure 3).

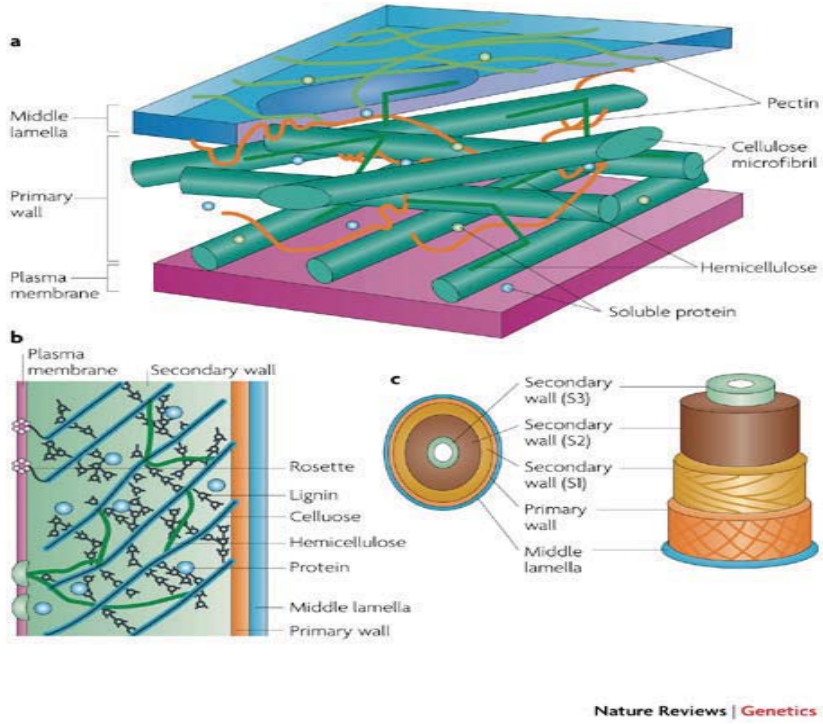

Figure 3. *Plant plasma membrane and cell-wall structure.* ***a****) Cell wall containing cellulose microfibrils, hemicellulose, pectin, lignin and soluble proteins.* ***b****) Cellulose synthase enzymes are in the form of rosette complexes, which float in the plasma membrane.* ***c****) Lignification occurs in the S1, S2 and S3 layers of the cell wall (adapted from* Sticklen 2008*).*

The layered cell wall architecture of wood fibres (Figure 3c) consist of middle lamella, primary wall, and three secondary cell wall layers (S1, S2, S3). The primary wall is rich in hemicelluloses, pectin, and lignin. The bulk of cellulose exists in the secondary cell wall layers, especially in the thick S2 layer. Besides thickness, the secondary cell wall layers differ from each other in the orientation of the microfibrils along the fibre axis. S2 layer is considered as the main load bearing element in wood fibres and both the thickness and the microfibril angle of the S2 layer affect the mechanical strength of fibres (Burgert et al. 2002; Page et al. 1977).

In delignified and bleached softwood pulp fibres, the fibre material of interest in this thesis, most of lignin (middle lamella), extractives, and part of the hemicelluloses are removed in the pulping process. The remaining pulp fibres are rather pure in cellulose; containing about 70-80% of cellulose and 20-30% of hemicelluloses (Gullichsen & Paulapuro 2000). Before a ready paper product, like the page of this printed book, the native wood fibres would have to undergo severe mechanical, chemical, and thermal treatments that influence the chemical and physical properties of the fibres. The desired properties of this page thus emerge from the combined effects of raw materials, processing, and additives.

2.1.1 Fine structure of fibre surfaces

The fibrillar structure of wood fibre surfaces have been studied by several microscopic techniques (Duchesne & Daniel 1999). However, when considering the fibre surface as a hydrated gel-like structure of cellulose microfibrils (and associated wood polymers), the characterization of wood fibre ultrastructure *in situ* and the imaging of cell wall surface of a never-dried pulp fibre are challenging tasks. Cellulose fibres are highly hydrated in the never-dried and rewetted states, and most sample preparation methods for microscopic imaging require direct drying or other means of dehydration; therefore, the obtained images do not necessarily represent the native structure. Because cellulose microfibrils tend to form aggregates inherently, during drying, and within fibre processing (Billosta et al. 2006; Duchesne & Daniel 2000; Hult et al. 2001), special caution is required when probing into the fibre surface structures by different methods. An image of kraft pulp fibre surface in the never-dried state by a cryogenic scanning electron microscope (cryo-SEM) is presented in Figure 4, showing the swollen aggregated fibrillar structures.

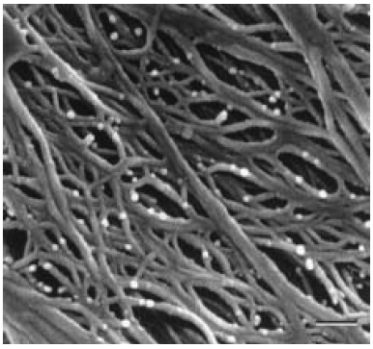

Figure 4. *High resolution cryo-SEM image of the surface ultrastructure of a frozen hydrated kraft pulp fibre. The swollen macrofibrils are locally agglomerated into small bundles. Bar=100 nm (Adapted from* Duchesne & Daniel 1999*).*

Images of different cell wall layers of never-dried bleached pulp fibres by transmission electron microscopy (TEM) technique are presented in Figure 5. It is easily conceivable that the interactions within and between these fibrillar surface structures are of prime importance for fibre bonding and strength in paper. Also, when considering the effects and the mechanisms of action of paper strength additives, the interactions of the polymers with the fibrillar fibre surfaces are the key to understanding. Unfortunately, the structural and chemical heterogeneity of cellulose fibres excludes the direct use of several sophisticated techniques for studying the adsorption, adhesion, chemical composition, structure, or other physical and chemical properties. Therefore, model fibrillar surfaces and fibril materials have been developed and successfully applied in cellulose research, as demonstrated in the next section.

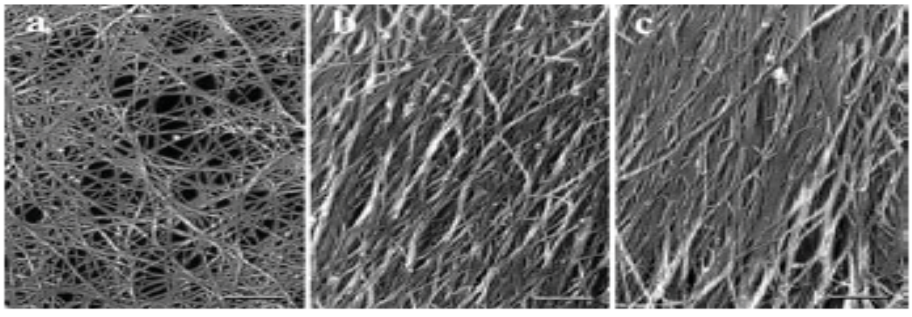

Figure 5. *Ultrastructural morphology of typical cellulose fibril aggregates within different cell wall layers of bleached pulp fibres.* ***a****) Primary cell wall;* ***b****) S1 layer;* ***c****) S2 layer. The random orientation of the fibrils in the primary cell wall contrasts greatly with that seen in the S1 and S2 layers. Note the more compact texture of the S2 layer. Bar =400 nm (Adapted from* Bardage et al. 2004*).*

2.1.2 Model materials in cellulose research

The development of cellulose model surfaces have enabled studies on the adsorption and adhesion phenomena and on the molecular level interactions between materials by sophisticated techniques, like SPR, QCM-D, and AFM, which all require well defined, smooth, and covering substrate surfaces (Kontturi et al. 2006). Recent comprehensive work on cellulose nanofibrils prepared from wood pulp fibres showed that the cellulose nanofibril model surfaces were a good representation of the fibre surface (see Figure 6), having similar fibrillar morphology, chemical composition, and crystalline structure (Ahola 2008). Part of that work, adsorption studies of polymers on cellulose nanofibril model surfaces, is included in this thesis (Paper II).

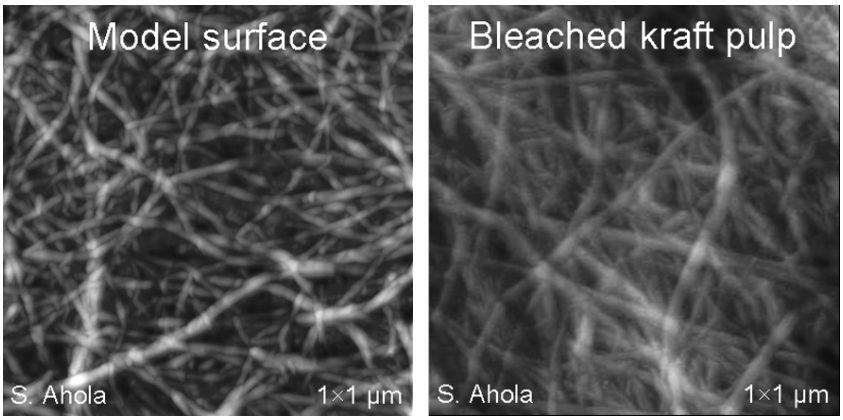

Figure 6. *Comparison between the cellulose nanofibril model surface and the fibrillar surface of a pulp fibre (AFM images presented by courtesy of Susanna Ahola).*

Together with environmental awareness, the increased interest in bio-based materials and fuels has boosted the research on cellulose in many disciplines. For example, in the field of composite materials, the advantageous properties of cellulose – renewability, biodegradability, biocompatibility, high specific strength, and non-abrasive nature – have been noticed. Much research has been performed to develop new ways to produce fibrillar cellulosic substances and cellulose whiskers from different raw materials, to develop novel bio/nano composite materials, and to tailor the materials to desired applications (Samir et al. 2005; Berglund 2005; Hubbe et al. 2008; Kramer et al. 2006).

Along with the innovation of novel engineering materials, the research on cellulose composites can also give new insight into the structure and properties of cellulosic materials. Analysis of composite structure and properties can provide information on the interactions, adhesion, and compatibility between the components (Hussain et al. 2006). Biomimetic materials are a good example where nature's ability to create controlled hierarchical structures is imitated in order to gain insight in structure-function relationships e.g. in the wood cell wall (Chanliaud et al. 2002; Dammström et al. 2009; Jean et al. 2009; Salmén & Burgert 2009; Somerville et al. 2004; Svagan et al. 2007). In this study, a similar approach to fibre bonding, by looking into the structure and properties of MFC-polymer composites (Paper IV), was adapted. In particular, the target was to understand the influence of strength additives on fibre bonding by acquiring information on the compatibility, interfacial properties, and the viscoelastic behaviour of cellulose microfibrils and polymers in composite structures.

2.2 Polymer adsorption onto cellulose fibres

The phenomenon of polymer adsorption is of great scientific and industrial relevance in the fields of paper, food, and pharmaceutics, just to name a few. It is also a very complicated phenomenon and will not be reviewed here. For comprehensive theoretical considerations of polymer adsorption, the reader is referred to a publication by Fleer et al. (1993).

In papermaking, a large variety of polymers are applied for the purposes of retention, strength, sizing etc. Because pulp fibres are anionic in water, the polymeric additives are usually modified to be cationic in order to provide high efficiency in the wet end application on a paper machine. The important polymeric properties for papermaking additives, from the viewpoint of function or efficiency, include molecular structure, molecular mass, reactive and charged groups, and charge density (Allan et al. 1978; Pelton 2004; van de Ven 2000; Wågberg 2000). The adsorption of charged polymers onto cellulose fibres and its kinetics have been exhaustively studied experimentally and theoretically (van de Ven 2000; Wågberg 2000; Wågberg & Hägglund 2001; Ödberg et al. 1993). Pure electrosorption, i.e. adsorption by electrostatic affinity and stoichiometric ion exchange, was found to govern the adsorption of most cationic

polyelectrolytes (Wågberg 2000; Ödberg et al. 1993). The kinetic studies emphasized the importance of the reconformation of polymers on surfaces with time (Ödberg et al. 1993). Depending on the molecular size of a polyelectrolyte, its accessibility into the fibre wall is different. Small molecules can fully penetrate the fibre wall whereas large molecules are constrained to the outer surface of the fibres; therefore, polyelectrolyte adsorption has been widely used as a method to assess the charge and porosity of cellulose fibres (Horvath et al. 2006; van de Ven 2000).

Not all polymers require cationic charge in order to adsorb onto cellulose. In particular, several neutral or even anionic polysaccharides are substantive to cellulose and can be irreversibly adsorbed onto cellulosic substrates. Water soluble cellulose derivatives, vegetable gums, and hemicelluloses, are adsorbed onto fibres in the absence of electrostatic interactions (Howard et al. 1977; Ishimaru & Lindström 1984; Laine et al. 2000; Swanson 1950). The adsorption mechanism of certain neutral polysaccharides has been attributed to specific structural interactions of the polymers with cellulose (Mishima et al. 1998). This is reasonable seeing that hemicelluloses, such as xyloglucans, are intimately associated to the fibre wall structures already during the biosynthesis of wood (Somerville et al. 2004). Utilization of the specific non-electrostatic interactions of polymers with cellulose has generated novel methods of surface modification of cellulose and promising applications in the paper, polymer, and composite fields (Klemm et al. 2009; Laine et al. 2002; Seifert et al. 2004; Zhou et al. 2007).

Polysaccharides that are substantive to cellulose are, indeed, very good strength additives for paper (Lindström et al. 2005; Swanson 1956). However, their application has not been feasible for two main reasons. Firstly, the polymers are expensive and the gain in properties would not cover the cost in comparison to just adding more of a conventional additive, like starch. Secondly, neutral polymers, due to slower adsorption kinetics and lower adsorption efficiencies, are hardly suitable for wet end addition in the papermaking process. In the case of carboxymethyl cellulose (CMC), the latter constraint has been circumvented by modifying the fibres during pulping or bleaching, i.e. prior to the paper machine's wet end (Kontturi et al. 2008).

The classic way to study polymer adsorption onto cellulose fibres is done by measuring adsorption isotherms and kinetics, and the effects of salinity and pH conditions on them. All studies have indicated the importance of the polymer conformation on the fibre surface but there has not been any method available for such a direct measurement (Wågberg 2000). To date, to the author's knowledge, there still does not exist a method to directly probe the conformation of an adsorbed polymer on an individual cellulose fibre in water. Instead, the utilization of cellulose model surfaces with surface sensitive techniques, like AFM, SPR, QCM-D, and ellipsometry, has provided invaluable information on the conformation and on the interactions of polymers on cellulose surfaces. The model surface studies are of great help in explaining the influence of polymers on fibre suspension and paper properties (Ahola et al. 2008b; Salmi 2009). Some of the aforementioned techniques were successfully implemented in Papers II and V.

2.3 Paper strength additives

On a paper mill, before the fibres are fed to the paper machine, there is a crucial process stage in regard to paper strength, viz. refining. Refining is an energy-intensive mechanical process which considerably improves fibre bonding and results in stronger paper. The mechanism of refining in improving fibre bonding and paper strength has been related to fibre swelling, plasticization, fines generation, external fibrillation etc. (Emerton 1957; Kang & Paulapuro 2006; Kibblewhite 1973; Retulainen et al. 1993). However, paper strength additives have always been indispensable in papermaking. Though the strength additives have not been able to obviate refining, they have provided several advantages not attainable by refining.

Paper strength additives are commonly divided by purpose into dry and wet strength additives. Dry strength additives can be regarded as adhesives that improve bonding between fibres while wet strength additives are chemically reactive synthetic resins that require curing and covalent crosslinking to improve the strength of rewetted paper. Some strength enhancing polymers, relevant to this thesis, are classified below.

2.3.1 Natural polymers and their derivatives

Several polysaccharides that are commonly used as strength additives or have shown good potential as such materials include starches, cellulose derivatives, xyloglucans, galactomannans, and chitosan. Molecular structures of the polysaccharides are collected in Figure 7.

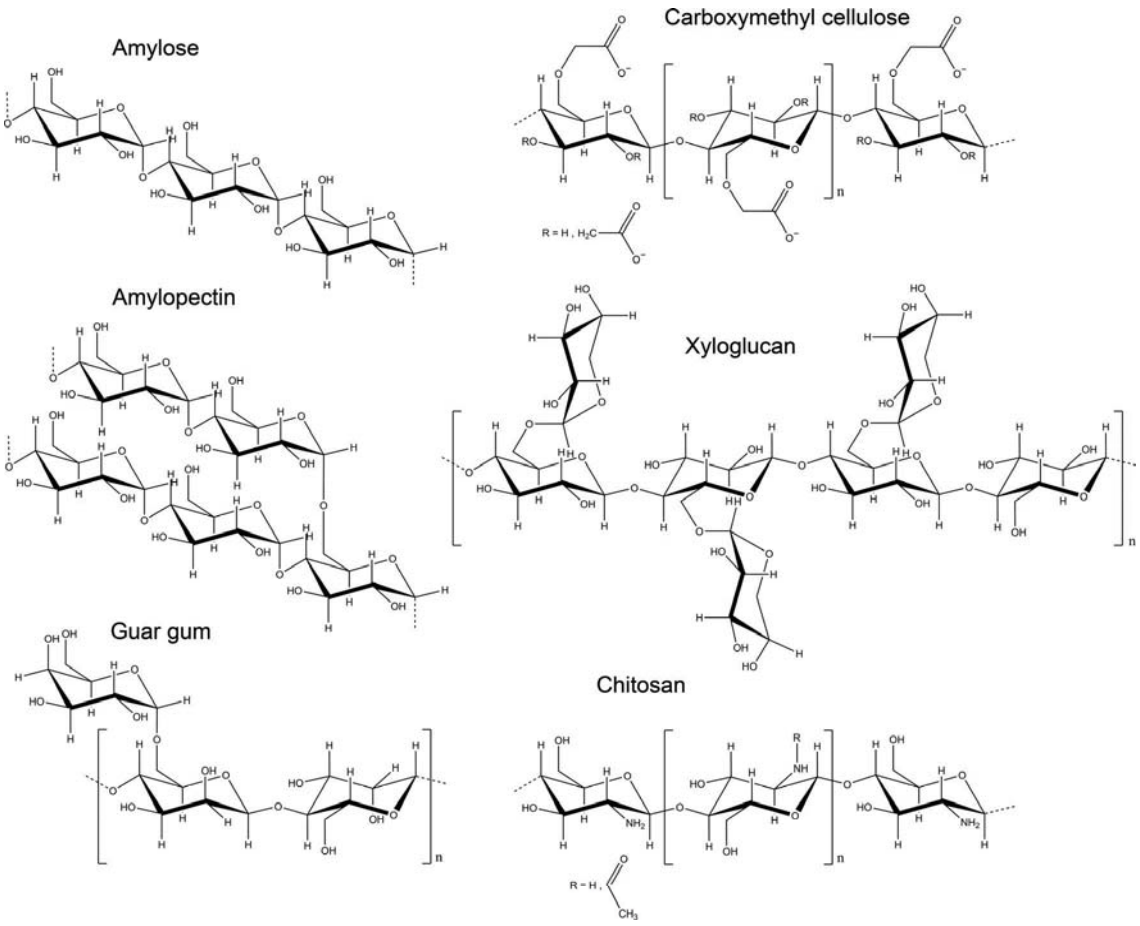

Figure 7. *The molecular structures of polysaccharides relevant to this thesis.*

Starch is widely utilized as a paper strength additive (Reynolds 1980). On a macromolecular level starch composes of two main polysaccharides; amylose and amylopectin (Fig. 7). Amylose is an essentially linear polymer of 1-4 linked α-D-glucopyranosyl units whereas amylopectin is a highly branched polymer of the same D-glucopyranosyl units with 1-4 linked α-D-glucopyranosyl chains branched by 1-6 linkages (Fig 7). The molecular weights of native amylose and amylopectin are in the range of 0.25 to 1 Mg/mol and 10-500 Mg/mol, respectively. Amylose content in starch as well as the branched structure of amylopectin depend on the plant species

(potato, corn etc.) (Dumitriu 2005). The amylose fraction of native starch adsorbs onto cellulose but very slowly (Pearl 1952). Thus, for wet end application starch is cationized, usually through addition of quaternary amine functional groups (Reynolds 1980). In addition, a variety of grades of starch additives for different purposes is prepared by other chemical modifications like hydrolysis and oxidation (Dumitriu 2005). Prior to use, starch needs to be cooked in order to obtain the desired solution properties. The solution properties of starch further influence the attained paper properties (McKenzie 1964).

Guar gum galactomannan. Certain vegetable gums, like locust bean gum, karaya gum, and guar gum, have shown excellent effects in improving paper strength and formation (Swanson 1950). Guar gum is a branched galactomannan polymer which has a linear 1-4 β-D-mannan backbone with 1-6-linked α-D-galactose side groups on approximately every second mannose unit (Fig. 7). The molecular weight of native guar gum is around 0.2 Mg/mol (Dugal & Swanson 1972). It adsorbs naturally onto cellulose fibres though it does not carry cationic charges (Swanson 1950). The interaction of the linear mannan backbone with cellulose has been proposed to cause the irreversible adsorption (Hannuksela et al. 2002).

Xyloglucans are an important group of structural polysaccharides in the plant primary cell wall (Somerville et al. 2004). Xyloglucans are composed of a linear 1-4 β-D-glucan backbone with 1-6-α-xylose residues (side groups), that can again carry galactopyranose, fucopyranose, and arabinofuranose residues (Dumitriu 2005; Zhou et al. 2007). Xyloglucan from tamarind, a commercial product, has only xylose residues on the 1-4 β-D-glucan backbone (Fig. 7). Xyloglucan is readily adsorbed onto cellulose fibres (Zhou et al. 2007) and is known to act as a crosslinking polymer for cellulose fibrils in the primary cell wall structure (Somerville et al. 2004; Whitney et al. 2006). Xyloglucan is known to improve both paper strength (Ahrenstedt et al. 2008) and sheet formation (Yan et al. 2006). Like CMC, xyloglucan was found to decrease the friction between cellulose surfaces, accounting for the improvement in paper formation (Stiernstedt et al. 2006). The strength improvement was related to the specific interaction between xyloglucan and cellulose (Ahrenstedt et al. 2008). For a bulk paper strength additive xyloglucan is expensive, but it has shown potential as a sophisticated method of cellulose modification (Zhou et al. 2007).

Chitosan is a natural linear aminopolysaccharide of 1-4 β-D-glucosamine derived from chitin by deacetylation. Chitin (linear 1-4 β-N-acetyl-D-glucosamine polysaccharide) exists mainly as a structural polymer in the shells of crustaceans. Generally, chitosan itself is not a well defined polymer but rather a class of polymers, chitin derivatives, with a degree of deacetylation over 70% (Rinaudo 2006; Rosca et al. 2005). In papermaking, chitosan has shown potential as dry and wet strength agents (Allan et al. 1978; Lertsutthiwong et al. 2002). In addition, chitosan is one of the few polymers known to improve the strength of a wet paper web before drying (Laleg & Pikulik 1991). The structural similarity of chitosan to cellulose (see Fig. 7) and electrostatic attraction are considered to induce a strong interaction between the polymers. These interactions and the possibility of chemical reactions between the reactive groups of the polymers have been proposed as explanations for the mechanism of action of chitosan as a papermaking additive (Laleg & Pikulik 1992; Li et al. 2004).

Carboxymethyl cellulose (CMC) is a widely applied cellulose derivative prepared by etherification of cellulose (Dumitriu 2005). CMC is produced in variety of molecular weights and degrees of substitution, influencing its solubility and solution properties. CMC along with several other cellulose derivatives can be adsorbed irreversibly onto cellulose fibres (Howard et al. 1977; Ishimaru & Lindström 1984; Laine et al. 2000; Shriver 1955). Adsorption of CMC onto cellulose requires suppression of the electrostatic repulsion between anionic CMC and the fibres (Laine et al. 2000). Fibres modified by CMC have shown excellent dry strength properties in unfilled paper sheets, and the mechanism of action of CMC as a strength additive has been discussed (Blomstedt et al. 2007; Duker & Lindström 2008; Laine et al. 2002). Furthermore, CMC is known to improve paper formation by dispersing the fibre suspension (Liimatainen et al. 2009; Yan et al. 2006), which has been related to reduced friction between CMC modified cellulose surfaces (Horvath & Lindström 2007; Yan et al. 2006; Zauscher & Klingenberg 2001).

2.3.2 Synthetic polymers

Synthetic polymers that are used as strength additives in papermaking include e.g. poly(acrylamide), polyvinylamine, and different wet strength resins: urea-formaldehyde (UF), melamine-formaldehyde (MF), and poly(amideamine) epichlorohydrin (PAE) resins (Chan 1994; Espy 1995; Reynolds 1980). Cationic poly(acrylamides) (C-PAM) are prepared by radical co-polymerization of an acrylamide monomer with a cationic charge carrying comonomer (Fig. 8). The polymers can be prepared in ranges of molecular weights and charge densities depending on the use (strength, retention). Synthetic polyampholytes and polyelectrolyte complexes of poly(acrylamides) and other polyelectrolytes have also shown potential as strength additives (Ankerfors et al. 2009; Hubbe et al. 2007; Vainio et al. 2006). Polyvinylamine (PVAm) is a linear amine functional polymer (Fig. 8) known to improve both the wet and dry strength of paper (DiFlavio et al. 2005). Wet strength resins are chemically reactive condensation products of urea-formaldehyde, melamine-formaldehyde, and poly(amideamine) epichlorohydrin (Fig. 8), that impart permanent wet strength to paper after drying and curing.

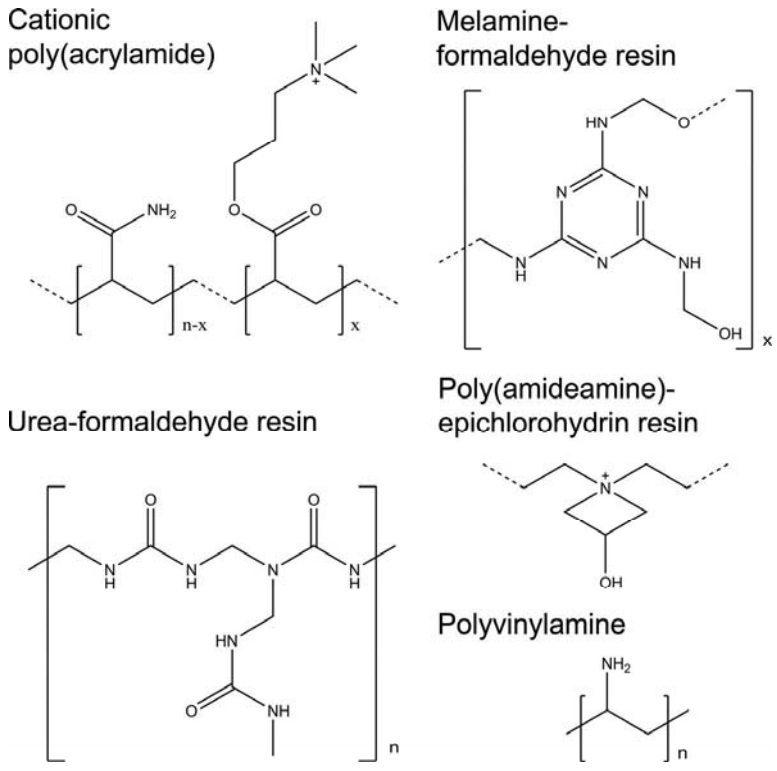

Figure 8. *Schematic molecular structures of synthetic strength additives.*

2.4 The mechanical properties of paper

The strength properties of paper, or any material, are extremely important for manufacturers and end-users, as well as in recycling. Tensile, tear, and internal strength of paper are standard measures for the mechanical properties of paper products. Still, when considering the mechanism of action of different strength additives, these measures give only the ultimate strength effect of an additive on the dry paper properties. Thus, no information how the strength properties develop from wet sheet to dry paper is obtained. Wet web strength, in particular, is important for paper production as web breaks typically occur at the early stages of papermaking process where the paper web is moist and very weak compared to dry paper. However, relatively little information is available on the effects of different strength additives on the development of paper strength during the early stages of drying.

2.4.1 Dry and wet strength mechanisms

Fibre bonding, paper strength, and the utilization and effects of different dry strength additives on paper properties have been recently comprehensively reviewed (Hubbe 2006; Lindström et al. 2005). Also, the dry strength of paper has been considered from the viewpoint of the most important polymer properties in regard to paper strength (Pelton 2004). The pioneering studies on fibre bonding (Ingmanson & Thode 1959; Thode & Ingmanson 1959; Van den Akker 1959), wet web strength (Lyne & Gallay 1954), cellulose fibre structure (Emerton 1957), and paper strength (Page 1969) have been indispensable as foundations for the materials science of paper. Yet, after innumerable studies on the effects of strength additives on paper properties, the underlying mechanisms of paper strength development and the function of strength additives are still somewhat unclear.

Recently, the concept of fibre bonding has evolved as the complex structure-property relationships of cellulose fibres and fibrils have been examined from the molecular level onward (Billosta et al. 2006; Duchesne & Daniel 2000; Hult et al. 2001). Hubbe (2006) differentiated between the conventional and the molecular level views of fibre bonding, as presented in Figure 9. In the new approach to fibre bonding, the molecular

level interactions between fibres and strength additives have been stressed as crucial contributors to the development of fibre bonding and paper strength (Eriksson 2006; Torgnysdotter 2006).

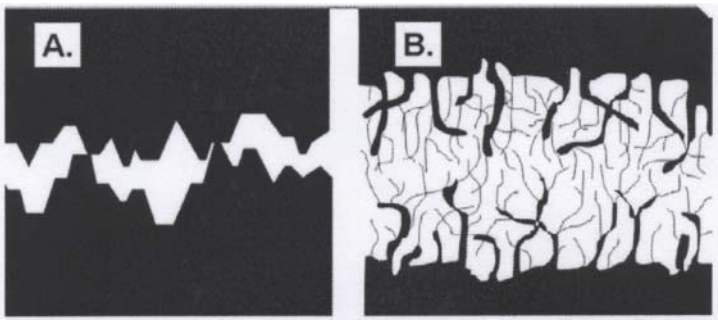

Figure 9. *Contrasting schematic concepts of contact between real solid surfaces. A: Conventional view. B: Fibrillated surfaces in the wet condition. (Adapted from* Hubbe 2006*).*

The mechanisms of action of wet strength additives have been discussed in many publications (Espy 1995; Wågberg & Björklund 1993). Generally, the division between self-condensing resins (UF and MF resins) and hetero-crosslinking polymers, like PAE and glyoxal-, aldehyde-, and epoxide-functional polymers that also react with cellulose, is well grounded. The self-condensing resins are believed to act by a protective mechanism, i.e. the resin forms a water insoluble crosslinked network that preserves some fibre bonding when the paper is rewetted. Wet strength additives in the latter group are able to form covalent bonding between the functional groups of the polymers and cellulose, thus they are able to reinforce the natural bonding of fibres. Expectedly, the reinforcing mechanism also include the self-crosslinking of the polymers, at least to some extent, since the crosslinking reactions are not selective to cellulose. The water resistant covalent bonding adds to the natural bonding of fibres and improves the cohesive strength of rewetted paper (Espy 1995; Wågberg & Björklund 1993). However, the wet strength mechanisms of polyamines including PVAm, poly(ethyleneimine) (PEI), and chitosan have yet to be scrutinized. In detailed studies on PVAm, the improvement in the initial wet strength of paper has been related to increased wet adhesion between fibres by covalent bonding and electrostatic interactions (DiFlavio et al. 2005).

Overall, the seminal research and present knowledge on cellulose fibre and fibril structure, on paper strength, and on the function of polymeric strength additives combined with novel approaches to fibre bonding and paper structure (Eriksson 2006; Torgnysdotter 2006) promise further insight into the mechanisms behind strength in cellulosic materials.

2.4.2 Strength development and drying effects

According to the classic work by Lyne and Gallay (1954) the strength of a wet paper web is controlled by two mechanisms: At low solids (below 20%) the strength originates from surface tension forces and mechanical entanglement and friction between fibres. At solids above 25%, interfibre bonding begins to dominate the strength development. The influence of the surface tension of water has been considered important for the wet strength of paper (Campbell 1959; Lyne & Gallay 1954; van den Akker 1959). More recently, entanglement friction has been pointed out as a crucial contributor to wet strength (de Oliveira et al. 2008; van de Ven 2008). Still, very little information is available on the effects of different polymers on the development of paper strength from a wet sheet to a dry paper. For instance, chitosan has been found to increase wet web strength throughout the measured solids range (Laleg & Pikulik 1991; Laleg & Pikulik 1992), and work by Mesic (2002) indicated that the strength development depended on the polymer used (Figure 10).

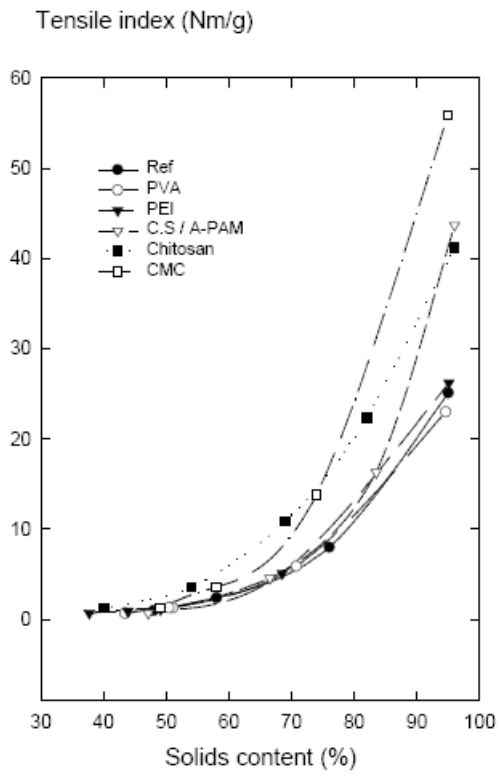

Figure 10. *Effects of various chemical treatments on the development of the tensile index of bleached kraft pulp vs. solids content. The following chemical additives were used: open squares CMC (17 mg/g attached), filled squares chitosan (17 mg/g attached), open circles PVAm (0.5 mg/g added), filled triangles PEI (0.5 mg/g added), open triangles CS / anionic PAM (50 mg/g / 1.5 mg/g added). (Adapted from* Mesic 2002*).*

The ultimate strength of paper is very sensitive to drying conditions. By controlling the shrinkage of a drying paper, considerable changes in the tensile properties can be obtained (Wahlström & Fellers 2000). For example, tensile stiffness of paper is affected by the applied restraints during drying (Blomstedt et al. 2007). Otherwise, there are very little studies on how the different strength additives respond to different drying conditions. Presumably, these types of studies could enable optimization of polymer dosing and drying conditions for a certain additive in regard to the desired end properties of a paper product.

3 EXPERIMENTAL

This chapter gives a short introduction to the materials and methods relevant to this thesis. More detailed experimental descriptions are presented in Papers I-V. An overview of the main methodology with supporting information and simplified illustrations are provided.

3.1 Materials

3.1.1 Cellulose fibres

Bleached pine kraft pulp obtained from Botnia (Äänekoski, Finland) was used in the experiments. The pre-processing of the fibre material depended on the experiments for which the fibres were used. Common preparation steps for all fibre samples were refining to a desired level, removing of fines, and washing to sodium counter-ion form. The fines removal and subsequent washing steps were done equally throughout the experiments. Shortly, the fines were removed by flushing the refined pulp suspension in a stirred tank with a wire sieve bottom and constant flow-through of fresh tap water. Thereafter, the fibres were washed into sodium counter-ion form according to procedure by Swerin & Wågberg (1994). The washed pulp samples were preserved in a refrigerator.

For sheet experiments in Paper I, the fibres were refined in a Valley beater for 5 min in order to promote fibre bonding and polymer adsorption while aiming to keep the effects of polymers on the development of strength properties as discernible as possible. For the microscopic examinations in Paper I, the fibres were refined for 60 min to produce ample fibrillation of the fibre surfaces in order to observe the effects of different polymers on the dispersion/aggregation of fibre surface fibrils.

In Paper III, the fibre preparation was done in such a way that the interactions between the fibre surface fibrils and the adsorbed polymers would have as clear an

effect on bonding and strength development as possible. Therefore, to produce intact fibres with even surface fibrillation, a grinding method was chosen for the refining of the fibres. Adapted from a procedure by Kang and Paulapuro (2006), the pulp was ground with a Masuko Supermasscolloider (Masuko Sangyo, Japan). The grinding produced fines mainly from the primary and the S1 cell wall layers, and, after washing, even fibrillation on the secondary fibre wall was achieved without coarse fibre damage.

3.1.2 Cellulose microfibrils (MFC) and nanofibrils (NFC)

Cellulose microfibrils (MFC), used for the preparation of composite films in Paper IV, were prepared from the bleached pine kraft pulp obtained from Botnia (Äänekoski, Finland). The fibre preparation was the same as in Paper III, described above. Thereafter, the fibres were disintegrated into microfibrillar material by mechanical treatment adapted from Chacraborty et al. (2005). The fibres were refined in a PFI mill until the fibres were broken into a paste-like cellulose material. After dilution, coarse fibre fragments were removed by passing the suspension twice through a 200 mesh wire. Finally, the fibrillar suspension was passed through a high pressure laboratory homogenizer. The product, a suspension of cellulose microfibrils and bundles of microfibrils in water, was not as well dispersed and homogenous as the cellulose nanofibrils (NFC) used for the model surface studies (Paper II). However, from the viewpoint of the study, the disintegrated wood fibre cell wall was a good representative of the fibrillar material in the fibre bonding domain. Since the concept of microfibrillar cellulose (MFC) rather describes a class of materials that can be produced from several starting materials by different processes (see e.g. Dufresne et al. 1997; Taniguchi & Okamura 1998; Turbak et al. 1983; Yano & Nakahara 2004) than any exactly defined material, the term will be used herein as distinct from NFC.

Nanofibrillar cellulose (NFC) was produced at Innventia AB (Stockholm, Sweden). The preparation and characterization of the material have been presented elsewhere (Pääkkö et al. 2007). In brief, the NFC was prepared from never-dried bleached sulphite softwood cellulose pulp by mechanical and enzymatic treatments followed by high-pressure homogenization. Surface methods like QCM-D and SPR demand

nanometre-scale smoothness and thickness from the model surfaces used with the techniques. Therefore, the NFC was used as a starting material in the preparation of cellulose nanofibril model surfaces. The preparation and properties of the NFC model surfaces utilized in the adsorption experiments (Paper II) are described in detail in a related thesis work (Ahola 2008).

3.1.3 Polymers and other chemicals

Commercial polymer samples were used in all experiments (Papers I-V). Cationic starch (CS), Raisamyl 50021, was received from Ciba Specialty Chemicals (Basel, Switzerland). Carboxymethyl cellulose (CMC), Finnfix WRM, was provided by CP Kelco (Äänekoski, Finland). Medium molecular weight chitosan (Prod. no. 22742) was acquired from Fluka BioChemika (Buchs, Switzerland). Guar gum (G4129) was purchased from Sigma-Aldrich Finland (Helsinki, Finland) and tamarind seed xyloglucan from Megazyme (Wicklow, Ireland). Poly(diallyldimethylammonium chloride) PDADMAC was acquired from Allied Colloids Ltd (England) and cationic poly(acrylamide) (C-PAM), K3400R, was provided by Kemira (Helsinki, Finland). Mostly, the polymers were used as delivered, with two exceptions. The PDADMAC was fractioned by ultrafiltration using a cutoff >300 kg/mol for the molecular weight. The high molecular weight fraction of PDADMAC was used in the experiments (Paper II). Prior to the QCM-D and AFM experiments in Paper V, the chitosan was purified by a recrystallization procedure adapted from Baxter et al. (2005). Other applied chemicals were of analytical grade unless otherwise defined.

3.2 Methods

3.2.1 Preparation of paper and composite samples

Sheet preparation. Wet handsheets (60 g/m^2) were prepared in a laboratory sheet mould according to standard SCAN-C 26:76. Deionized water was used in the mould and $NaHCO_3$ was added to maintain a constant salinity of 0.5 mM. Handsheets were

then wet-pressed according to SCAN-C 26:76 except that the number of blotter paper sheets was reduced in order to decrease the initial solids for the measurement of strength development (Papers I and III).

Composite films. The composite films of cellulose fibrils and polymers (Papers I and IV) were prepared by a casting and evaporation method. Composite films with polymer content from 0 to 50% were made for tensile testing and dynamic mechanical analysis (DMA). The materials used and the preparation method varied somewhat among the experiments (for details, see Papers I and IV). In all cases, polymer solutions of 5 g/L were prepared and mixed with the fibril suspensions (0.5 wt-%). After stirring for a desired time, the mixtures were degassed by vacuum and subsequently cast on aluminium or plastic dishes. The composites were dried slowly at near-ambient conditions in order to avoid excessive shrinkage and unevenness of the films.

3.2.2 Measurement of paper strength development during drying

The development of paper strength during drying (Papers I and III) was measured with an experimental setup that consisted of a MTS 400m tensile tester (MTS Systems, USA) combined with an infra-red drying module (Hedson Technologies, Sweden) and an online moisture sensor (MM55E, NDC Infrared Engineering, USA). A schematic presentation of the method is shown in Figure 11. At first, 50 mm wide strips were cut from the wet pressed sheets. Before clamping the samples to the tensile tester, the sample ends were dried, leaving a 70 mm wet section as the effective wet testing length (Fig. 11a). After the specimen was clamped, all the tests were done as follows. The wet sample was dried from front side with the IR for a desired time (Fig. 11b). The moisture content of the sample was measured with the moisture sensor (Fig. 11c) and the tensile test was performed without delay (Fig. 11d). The tensile test was done according to ISO 1924-2, except that specimen dimensions were 50 mm × 70 mm and crosshead speed was 20 mm/min. The moisture sensor was calibrated with the particular fibre materials in both test series and its response was linear in the calibration range.

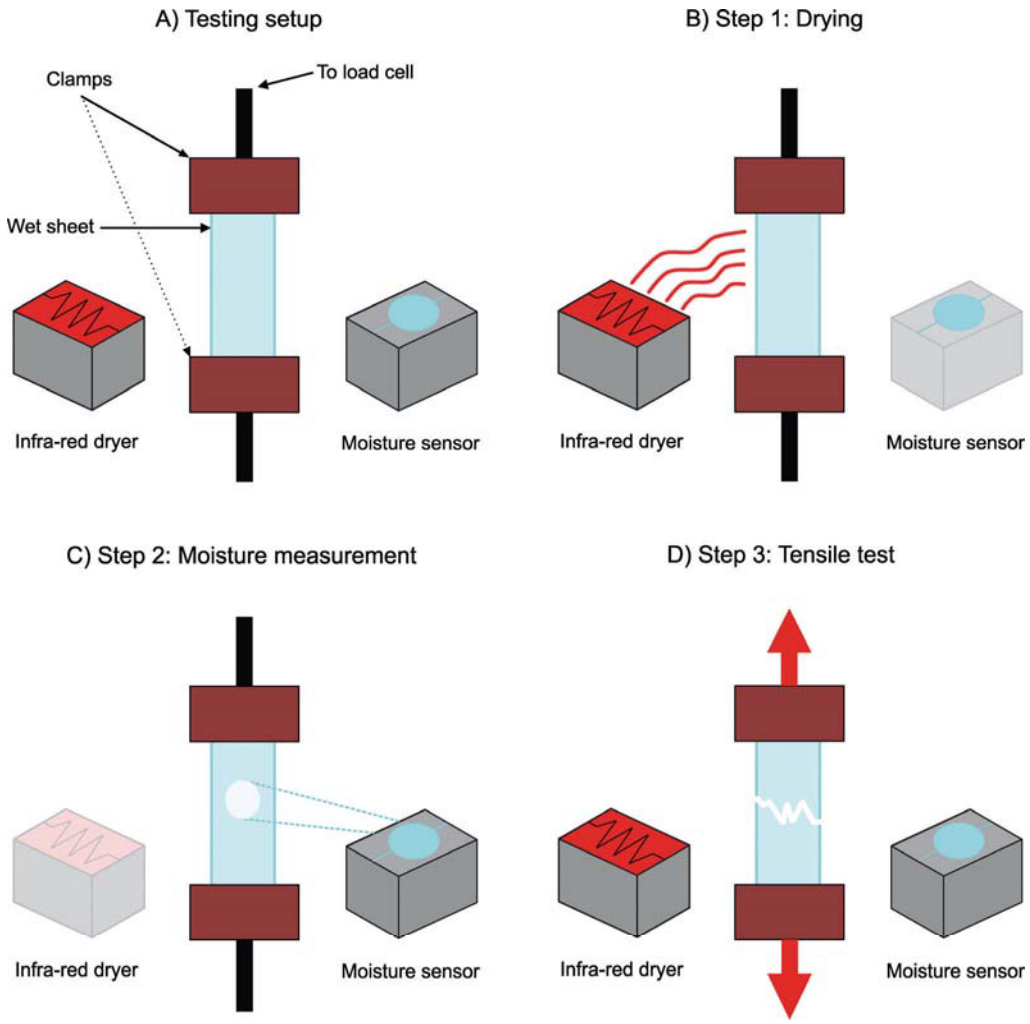

Figure 11. *A schematic of the measurement method for the development of tensile properties upon drying showing the setup (**a**), and the different measurement steps of drying (**b**), moisture measurement (**c**), and tensile test (**d**).*

3.2.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is a non-destructive analytical technique in which an oscillating stress is applied to a specimen and the resulting oscillating strain response is monitored. The strain response can be measured as a function of temperature and of frequency. If a specific environmental chamber is used in the DMA equipment, the testing can be conducted under different conditions – immersed in liquids or at controlled relative humidity (R.H.). Figure 12 shows a schematic of the DMA technique. DMA is a powerful tool for studying the viscoelastic behaviour of plastics and composite materials. For example, storage and loss moduli, glass transition

temperatures, curing reactions, and gelling in different polymeric materials can be measured with DMA (Foreman & Blaine 1997; Jones 1999). In addition, DMA can provide information on the interactions and compatibility between polymers in blends or between matrix and filler in composite materials (Dammström et al. 2005; Samir et al. 2004).

In a typical DMA measurement, storage modulus (E'), loss modulus (E''), and phase angle tan(δ) are followed as a function of temperature or of frequency. The storage modulus (E') represents an elastic strain response of the tested material, which, for an ideal elastic material, would directly follow the applied oscillatory strain (phase angle tan(δ) = 0°, see Fig 12). The loss modulus (E'') represents a viscous response in the material, which, for an ideal Newtonian fluid, means that the strain response lags the stress by 90 degrees. For viscoelastic materials the phase angle is between these limits. The storage modulus (E'), when measured in tension, is similar to Young's modulus obtained by destructive mechanical testing methods (Foreman & Blaine 1997). The loss modulus (E'') and the damping factor tan(δ) have been considered as sensitive and accurate indicators of glass transition temperature(s) of polymeric systems (Hatakeyama & Liu 1998).

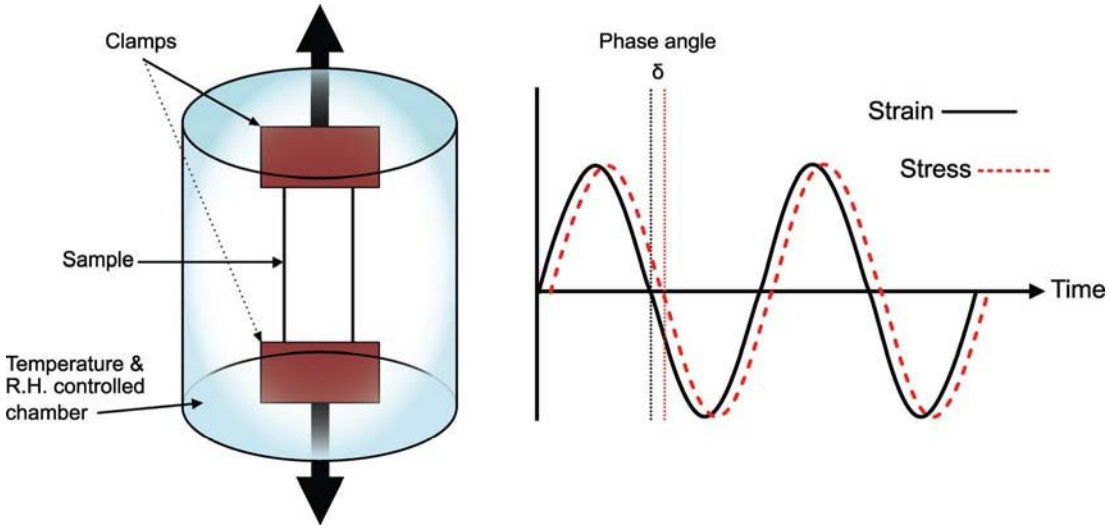

Figure 12. *A schematic of the DMA measurement setup and the principle of the technique.*

In contrast to common thermoplastic polymers and composites, polysaccharides are plasticized by water and not as much by merely heat. Also, the transitions, like glass

transition temperature(s), are affected by moisture content (Salmén & Olsson 1998; Stading et al. 2001). Therefore, dynamic mechanical analysis with regard to the surrounding humidity was considered as the best approach to study the moisture plasticization and viscoelasticity in composite materials made of MFC and different polysaccharides (Paper IV).

DMA measurements. Dynamic mechanical analysis of the composite films (Paper IV) were conducted with a DMA7e instrument from Perkin Elmer (Shelton, CT, USA). The instrument was equipped with a controlled humidity generator from Setaram (Caluire, France). The sample specimens were rectangular strips of the composite films with dimensions of about 20×4 mm^2 and thickness of ~25 μm. The DMA measurements were performed in film tension mode, at a frequency of 1 Hz, as a function of relative humidity (R.H.) at a constant temperature of 30°C. Quantities measured were dynamic storage modulus (E'), dynamic loss modulus (E''), and phase angle tan(δ). In order to compare the plasticization behaviour of different samples, relative modulus values were recalculated from the dynamic storage modulus (set to 100% at 30% R.H.) of each tested material.

3.2.4 Quartz crystal microbalance with dissipation (QCM-D)

Adsorption of polymers on cellulose model surfaces was studied with a quartz crystal microbalance with dissipation (QCM-D). The QCM-D technique enables simultaneous measurement of both the adsorbed amount of polymer on a sensor surface and the viscoelastic properties of the adsorbed polymer layer. The sensor is a quartz crystal that oscillates at a certain resonant frequency (f_0). The frequency changes on adsorption to a lower value (f), as the coupled mass on the surface increases. Provided that the adsorbed layer is uniform and rigid, the adsorbed mass per unit surface (Δm) is proportional to the change in frequency (Δf), according to the Sauerbrey equation (Höök et al. 1998; Sauerbrey 1959):

$$\Delta m = -\frac{C\Delta f}{n} \qquad (1)$$

where n is a number of the overtone of the sensed frequency and C is a sensitivity constant for the device. The relation is valid when the adsorbed mass is small compared to the mass of the sensor crystal.

By following the dissipation of energy during one cycle of oscillation, information on the viscoelastic properties of the adsorbed layer can be obtained. If the adsorbed layer is rigid (ideally elastic) there is no energy dissipated by viscous losses and the dissipation is not changed. However, in most cases, the adsorbed layer is not rigid but viscous, which causes dissipation of energy during oscillations. A dissipation factor D is defined as:

$$D = \frac{E_{diss}}{2\pi E_{stored}} \tag{2}$$

where E_{diss} is the energy dissipated in one cycle of oscillation and E_{stored} is the total energy of the oscillator. Information on the viscoelastic properties of the adsorbed layer is obtained from the change in dissipation (ΔD) during adsorption. The dissipation factor (D) is compared to the dissipation of the sensor surface in solution prior to adsorption (D_0). For a rigid adsorbed layer the ΔD is negligible, but for loose and viscous adsorbed layers ΔD increases with adsorbed amount. For a more detailed description of the technique and the interpretation of the QCM-D data the reader is referred to publications by the developers of the method (Höök et al. 1998; Rodahl et al. 1995; Sauerbrey 1959). Figure 13 shows a schematic of the QCM-D principle (Fig. 13a) and an example of the data obtained during an adsorption experiment (Fig. 13b).

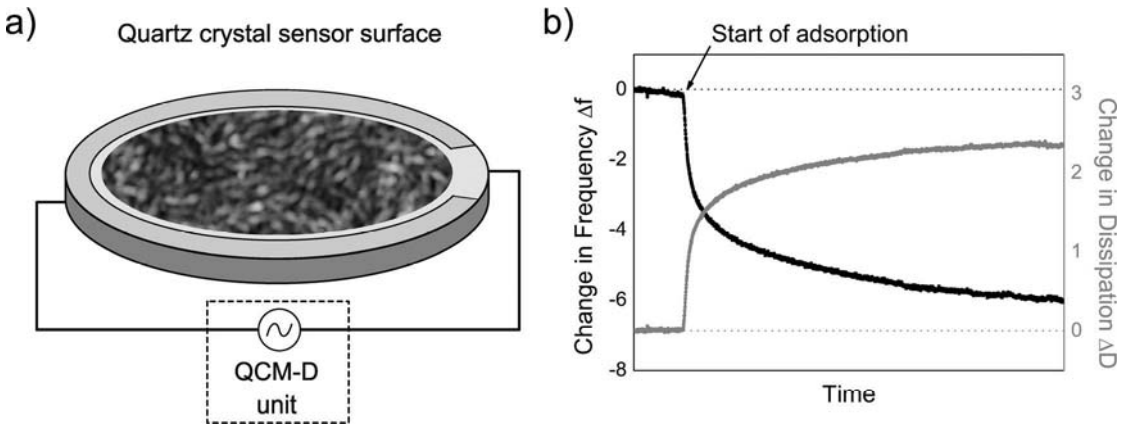

Figure 13. *Working principle of QCM-D (**a**) and example of the data obtained during an adsorption experiment (**b**).*

It should be emphasized that the QCM-D technique senses the overall increase in mass upon adsorption to the surface. It is not able to directly provide the dry amount of adsorbed polymer per unit surface because solvent molecules that are closely associated with the adsorbed polymer chains also add to the sensed mass. Thus, surface sensitive methods that are "blind" to the coupled solvent are good complementary techniques to be used in parallel with QCM-D.

QCM-D measurements. The polymer adsorption experiments (in Papers II and V) were carried out using a Q-Sense E4 QCM-D device, manufactured by Q-sense (Västra Frölunda, Sweden). In the study of the adsorption of different polymers on NFC model surfaces (Paper II), the QCM-D provided information on the adsorption behaviour of the polymers, on the viscoelastic properties of the fibril/polymer layer, and on the influence of polymers on the hydration of the nanofibril layer. In Paper V, the adsorption of chitosan on a Langmuir-Schaefer (LS) cellulose model surface and the viscoelastic properties of the cellulose/chitosan layer were monitored as a function of the pH of the surrounding solution by QCM-D. Preparation and properties of the model surfaces used are described in detail elsewhere (Ahola et al. 2008a; Tammelin et al. 2006).

3.2.5 Atomic force microscopy (AFM)

AFM imaging. The structure and morphology of cellulose model surfaces used in chitosan adsorption experiments (Paper V) were assessed by atomic force microscopy. AFM (Binnig et al. 1986) is a very high resolution microscopic technique that belongs to the class of scanning probe microscopic (SPM) methods. In AFM the scanning probe is a tiny sharp tip connected to a supporting cantilever. The sample surface is scanned by the tip, in a close proximity or in contact, and the interactions between the tip and the surface are recorded. The AFM imaging (Paper V) was performed with a Nanoscope IIIa Multimode scanning probe microscope from Digital Instruments Inc. (Santa Barbara, CA, USA). The images were scanned in tapping mode in air using silicon cantilevers. Sizes of the scanned images were 1x1 μm^2 and 5x5 μm^2. No image processing except flattening was made.

AFM Force Measurements. The scanning probe technique has been further developed for measurement of interaction forces between surfaces. The method, known as the AFM colloidal probe technique (Ducker et al. 1991), enables the characterization of interfacial forces between surfaces at different conditions and in the presence or absence of adsorbates. Hence, it is a powerful method to assess molecular level interactions, adhesion, steric effects, and conformation of adsorbed polymers. Here, the technique was applied to study the influence of pH of the surrounding solution on the conformation and adhesive properties of an adsorbed chitosan layer on a cellulose model surface (Paper V). For a detailed description of the method the reader is referred to work by Butt et al. (1991).

3.2.6 Other methods

Optical microscopy. The aggregating or dispersing effects of polymers on NFC suspensions and on fibrillation of fibre surfaces were studied by optical microscopy (Paper I). The fibrillated fibres and NFC agglomerates were observed and photographed with a Leica DM LAM microscope (Leica, Wetzlar, Germany) equipped with a Leica DC 300 digital camera. Note, that the NFC here refers to the

aggregated NFC suspension which is an opaque gel-like material. Thus, it was possible to observe the dispersion/aggregation of the NFC by optical microscopy.

Scanning electron microscopy (SEM). The instrument used in the scanning electron microscopic examination of the composite film structures (Paper IV) was a Hitachi S-4700 field-emission SEM (Hitachi High-Technologies, Krefeld, Germany). For cross-section imaging the composite films were cryo-fractured after immersion into liquid nitrogen. The SEM imaging of the cross-sections was done without a conductive coating on the samples.

Scanning electron microscopy of wet fibres (wet-SEM). The SEM images of wet fibres (Paper I) were obtained by using commercial Wet-SEM™ technology. The technique utilizes a special sealed capsule which separates the wet sample from the vacuum of the microscope chamber (Joy & Joy 2006; Thiberge et al. 2004). Wet fibre samples were placed into a QX-302 capsule to be viewed in the wet state. The wet fibres were imaged with the same SEM device as above.

Surface plasmon resonance (SPR). SPR was used to complement the QCM-D adsorption experiments in Paper II. The adsorption of PDADMAC and xyloglucan on NFC model surfaces was measured using a Biacore 1000 instrument with a continuous flow system (GE Healthcare, Sweden). The dry adsorbed amounts of polymers were calculated from the SPR results and compared to the total adsorbed mass from QCM-D measurements, thus making it possible to differentiate between the mass of polymer and the amount of associated water on the surface. The SPR technique is based on the phenomenon of total internal reflection of light, described in more detail by Schasfoort & Tudos (2008).

Tensile testing of composite films. Tensile testing was done with the MTS 400m tensile tester (MTS Systems, USA). The composite samples were tested according to the paper testing standard ISO 1924-2, except that the specimen length and width were 50 mm and 10 mm, respectively. The tensile tester was situated in a paper testing room with controlled climate (23°C, R.H. 50%) and all the samples were equilibrated under the atmosphere prior to testing.

Measurement of amounts of adsorbed polymers on paper samples. The amounts of adsorbed polymers applied as strength additives (in Paper III) were determined in a separate set of experiments. The adsorption experiments were carried out with 2 g of dry pulp in deionized water at a fibre consistency of 10 g/L. After the desired adsorption time, the sample was filtered through a filter paper and the polymer content of the filtrate was determined. The adsorbed amount of CS, xyloglucan, and guar gum was determined with sulphuric acid-phenol test (DuBois et al. 1956). Chitosan adsorption was determined with polyelectrolyte titration (Terayama 1952). The adsorbed amount of CMC was determined by conductometric titration (Katz et al. 1984).

4 RESULTS AND DISCUSSION

The most important findings during this thesis work are summarized within this chapter. The complete results are presented in the attached Papers I-V.

4.1 Interactions of polymers with cellulose fibrils

As a working hypothesis for this thesis, a new outlook to fibre bonding and paper strength was adopted in order to explain the interactions between strength additives and fibres, and to understand the mechanisms of strength development and the influence of the polymers applied. The adopted approach is based on the consideration of the wet fibre surface as a gel-like layer consisting of hydrated cellulose microfibrils (incl. other wood polymers) (Chapter 2.1.1, Paper I). Strength additives, when adsorbed onto the fibres, are mixed with the fibrillar gel-like surface layer of fibres and will influence the properties of the layer differently depending on the interactions between fibrils and polymers. Therefore, the wet web strength, strength development during drying, and the final properties of dry paper are affected by the interactions between the cellulose fibrils and the additives.

In order to gain more insight into the interactions between strength additives and fibres and how the interactions are reflected in fibre bonding and in the rheological properties of paper, the effects of polymers on fibre surface fibrillation and on NFC suspensions were studied at the microscopic (fibril aggregation/dispersion) and the macroscopic levels (paper sheets and model composite films) (Paper I). Information on the interactions at the molecular level was obtained by polymer adsorption experiments on NFC model surfaces with specific attention paid to the influence of hydration of nanofibrils and polymers as an essential factor regarding the properties of the gel-like fibril/polymer layer (Paper II).

4.1.1 Dispersion/aggregation of fibrils and fibrillated fibre surfaces

The aggregating or dispersing effect of polymers on the NFC suspension and fibrillated fibre surfaces were assessed by optical microscopy. Polymers can influence the level of aggregation of the fibril suspensions by dispersing or aggregating the fibrils. The native NFC suspension is inherently aggregated to some extent and forms microscopic flocs/aggregates (Fig. 14a), unless dispersed by specific means (e.g. ultrasound or chemical treatment). An aggregating polymer, like high molecular weight and low charged C-PAM, further aggregates the fibril suspension (Figure 14b). To the contrary, substantial dispersion of the fibril suspension was achieved by CMC adsorption (Figure 14c). The aggregating or dispersing effects of CS and chitosan (Paper I), and PDADMAC and xyloglucan (Paper II) on NFC suspensions were found to be somewhere between the presented extremes, as appreciated visually.

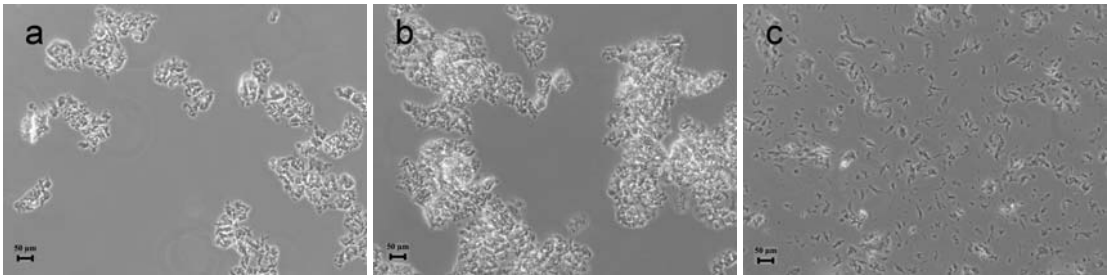

Figure 14. *Phase contrast images of plain fibril agglomerates (**a**), fibril agglomerates after C-PAM addition (**b**), and after CMC adsorption (**c**), bar = 50 µm. (Paper I)*

When comparing the aggregation/dispersion between the model fibrils (Fig. 14) and the fibrils on fibre surfaces (Fig. 15), the influence of C-PAM and CMC on the aggregation/dispersion was strikingly similar. Addition of C-PAM compacted the surface fibrils closer to the fibre wall and formed visible fibril agglomerates on the fibre surface (agglomerates circled in Fig. 15b). In contrast, the adsorption of CMC caused a notable dispersion and extension of the fibrillation on the fibre surface (Fig. 15c).

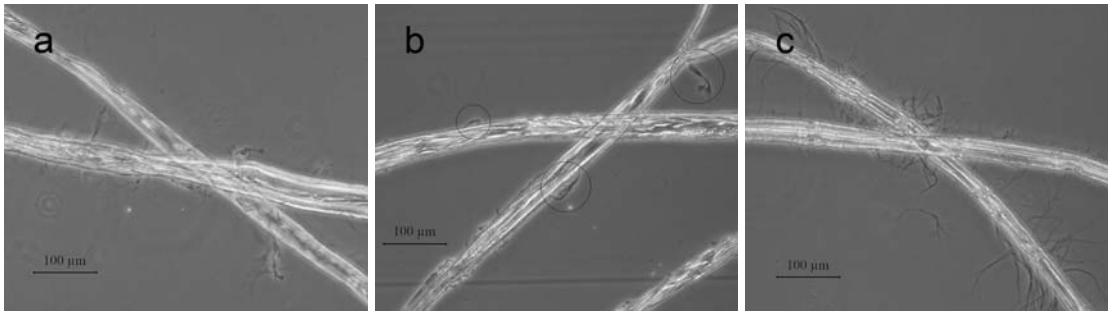

Figure 15. *Phase contrast images of plain fibres (**a**), fibres after C-PAM addition (**b**), fibres after CMC adsorption (**c**), bar = 100 µm. (Paper I)*

The optical microscopy images (Figs. 14 and 15) clearly describe the effect of aggregating and dispersing polymers on the native NFC suspension as well as on the fibrillar structure of the fibre surfaces. The appearance of fibre surface fibrillation after extended refining and removal of fines, in Fig. 15a, indicates that the fibrils and fibre wall remnants tend to agglomerate when liberated from the fibre wall by mechanical action, analogously with the observed aggregation tendency of NFC suspensions (Fig. 14a). The observations are supported by the findings that cellulose fibrils in the fibre wall tend to form aggregates within pulping and drying and that the aggregation is sterically controlled (Billosta et al. 2006; Hult et al. 2001). Similarly, both the NFC suspension (Fig. 14a) and the newly formed fibrils on the beaten fibres (Fig. 15a) were agglomerated in the absence of steric stabilization (e.g. by a dispersing polymer).

The aggregating effect of C-PAM mainly derives from electrostatic interactions between fibrils and the polymer. Electrostatic attraction drives the adsorption of the polymer on the fibril surfaces and at the same time the amount of bound water associated with the fibrils is reduced, making the fibril aggregates denser. However, the observed aggregation behaviour can not be accounted for solely by electrostatic interactions, due to a large difference between the charge densities of the materials. Because the polymer was of high molecular weight and low charge density, and thus able to induce bridging flocculation, the C-PAM produced larger fibril agglomerates (Fig. 14b).

The dispersing effect of CMC on the NFC suspension and on fibre surface fibrils depends on the method of adsorption of the polymer. After simple addition of CMC to the NFC suspension, the dispersing effect was hardly observed (see Paper II, CLSM images), whereas CMC adsorption, when carried out at high ionic strength, caused strong dispersion of the NFC suspension (Fig. 14c). The importance of the adsorption method of CMC has been pointed out in regard to fibre swelling and paper strength (Laine et al. 2002). In addition, the increase of specific surface of wet fibres by CMC adsorption has been shown earlier by microscopic methods (Blomstedt et al. 2007; Jokinen et al. 2006). Most likely, the adsorbed CMC breaks the weak bonding between agglomerated fibrils and induces electrosteric stabilization and, as a result, further disperses the NFC suspensions and fibre surface fibrils.

Composite materials are sensitive to the dispersion of the filler in the matrix as well as to the compatibility of components (Eichhorn et al. 2001; Hussain et al. 2006; Smits et al. 2008). Therefore, model composites prepared from native NFC and certain polymers were mechanically tested in order to attain indirect information on the aggregation/dispersion behaviour and on the interactions between the components. Furthermore, the properties of model composites may give information on the nature of fibre bonding in the presence of strength additives. Figure 16 exemplifies the influence of CMC, chitosan, and CS content on the strength of NFC-polymer composite films.

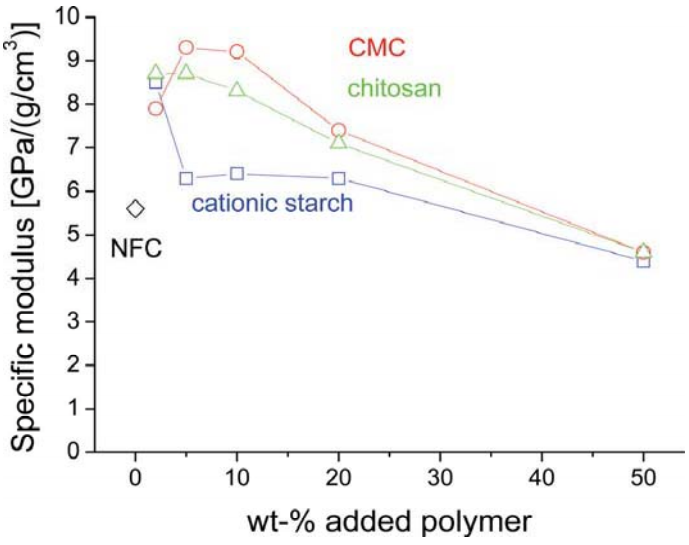

Figure 16. *Specific modulus of cellulose fibril – polymer composites. (Paper I)*

Clearly, small additions of polymers to the NFC suspension improve the composite strength. This is partly attributed to the improved dispersion of fibrils in the composite film because the ultimate strength of a film of pure cellulosic fibrils is very high (Henriksson 2008; Nakagaito & Yano 2005; Svagan et al. 2007). Secondly, the incorporation of polymer can decrease the porosity of the films and thus make the films structurally more coherent and more resistant towards crack propagation. In addition to the improved fibril dispersion and slight densification of the films, good compatibility between the materials (especially CMC) as well as water plasticization may affect the observed reinforcement. Indeed, moisture was found to have a strong effect on the strength of the tested composites. For example, Young's modulus of the CMC containing composite (10 wt-%) increased ~20% and the film became highly elastic when it was tested dry (unpublished results), as a contrast to testing at R.H. of 50%. The moisture plasticization of MFC-polymer composites and paper sheets is assessed in more detail in a separate study (Chapter 4.3, Paper IV).

4.1.2 Interactions of polymers with nanofibril model surfaces

The interactions of certain types of polymers with cellulose nanofibrils were studied by polymer adsorption experiments (Paper II). The adsorption of PDADMAC, CMC, and xyloglucan on NFC model surfaces was studied with QCM-D and SPR. Special attention was paid to the influence of polymers on the hydration of the nanofibril/polymer layer as an essential factor regarding the viscoelastic properties of the system.

The polymers studied were chosen on the grounds that they were known to interact with cellulose by different mechanisms. PDADMAC, a highly charged cationic polyelectrolyte, adsorbs on cellulose by pure electrosorption and can be used, e.g., as a fixative in papermaking suspensions (McNeal et al. 2005). Xyloglucan, a neutral polysaccharide, is known to adsorb on cellulose by virtue of specific molecular interactions with cellulose. The specific interaction has been suggested to derive from structural similarity of xyloglucan chain to cellulose and concomitant hydrogen bonding (Mishima et al. 1998; Zhou et al. 2007). CMC, an anionic cellulose derivative, can be irreversibly adsorbed on cellulose at certain conditions (Laine et al.

2000) but its adsorption is negligible at conditions where the electrostatic repulsion between CMC and cellulose is not screened. In addition, both CMC and xyloglucan are known to disperse cellulose fibre suspensions (Beghello 1998; Liimatainen et al. 2009; Yan et al. 2006). Thus, it was interesting to see whether the dispersing/aggregating effects observed on the microscopic and macroscopic levels (fibril and fibre suspensions) could be traced to molecular level phenomena at the polymer/nanofibril model interface.

QCM-D data on the adsorption of PDADMAC, CMC, and xyloglucan on cellulose nanofibril model surfaces is presented in Figure 17. The polymer solutions (100ppm) were injected to the system at the 10 min mark. The responses in frequency (Fig. 17a) and in dissipation (Fig. 17b) are related to the adsorbed amount of polymer and to the viscoelasticity of the fibril/polymer layer, respectively (Chapter 3.2.4). The adsorption of xyloglucan caused a decrease in frequency and an increase in dissipation, indicating that the polymer formed a loose, presumably hydrated, layer over the NFC model surface. The rinsing of the surface at the 250 min mark removed a small amount of excess xyloglucan from the surface, but the remaining polymer was irreversibly adsorbed on the nanofibrils (Fig. 17a).

The addition of CMC produced more gradual decrease in frequency and larger increase in dissipation in comparison to xyloglucan. At the conditions applied, CMC was not expected to adsorb on cellulose fibrils and, indeed, after rinsing the frequency and dissipation recovered to the starting level, indicating complete desorption of the polymer from the surface. It appears that CMC molecules were slowly associated with the fibril surface forming a very loose structure (high dissipation) and that the electrostatic repulsion between the anionic fibrils and CMC was strong enough to counteract the non-electrostatic specific interaction and to prevent irreversible adsorption of the polymer.

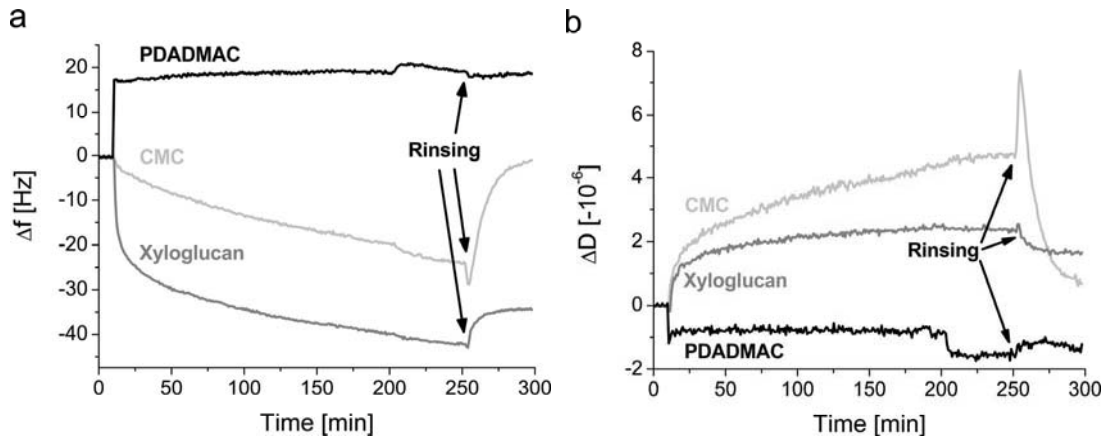

Figure 17. *QCM-D curves of* ***a****) change in frequency (Δf) and* ***b****) change in dissipation (ΔD) as a function of time during adsorption of xyloglucan, CMC, and PDADMAC on cellulose nanofibril model surfaces. (Paper II)*

In contrast to xyloglucan and CMC, addition PDADMAC induced a sharp increase in frequency and a decrease in dissipation, indicating a reduction of the detected mass and an increase in elasticity of the surface. Logically, the frequency response would suggest a removal of some of the fibrils from the surface by the polymer. However, this interpretation is ruled out by the facts that PDADMAC is known to adsorb on cellulose at the prevailing conditions in a rather flat conformation (Saarinen et al. 2009) by a stoichiometric charge ratio (van de Ven 2000), and that the adsorption of PDADMAC causes deswelling of fibres (Swerin et al. 1990). Here, the sharp increase in frequency is an indication of pure electrosorption of PDADMAC. The adsorption reaches equilibrium very quickly. Moreover, the apparent "desorption" most likely originates from removal of water from the swollen NFC surface due to charge neutralization. The dehydration of the NFC surface is consistent with the observed decrease in dissipation upon adsorption of PDADMAC.

In addition to the QCM-D experiments, the adsorption of the polymers was studied with SPR technique. The advantage of SPR over QCM-D is that it is insensitive towards the associated solvent molecules at the surface, and thus enables the determination of dry adsorbed amount of a polymer. However, the SPR has limitations in regard to modification of the sensor surface and to the adsorbates studied. Therefore, only the adsorption of xyloglucan and PDADMAC on NFC model surface was measured by SPR under the same experimental conditions as in the

QCM-D experiments. The dry adsorbed amount of the polymers as a function of time, derived from the SPR data, is presented in Figure 18.

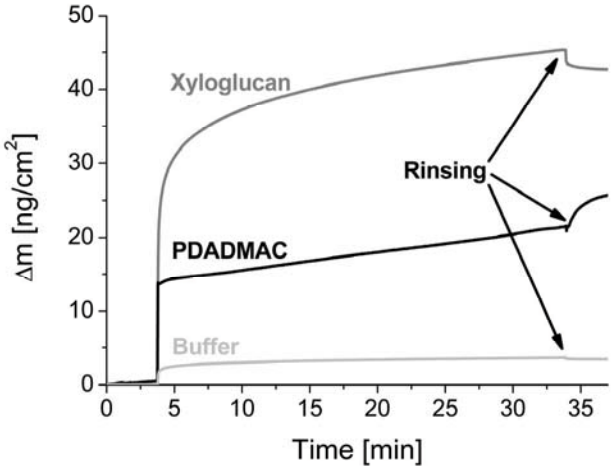

Figure 18. *SPR curves of xyloglucan and PDADMAC adsorption on cellulose nanofibril model surface. (Paper II)*

The SPR data verified the adsorption of PDADMAC, which was obvious but not undisputable by the QCM-D results alone. The adsorption profiles of the polymers are also similar to the ones seen in the QCM-D experiments, showing the rapid electrosorption of PDADMAC. The dry adsorbed amounts of PDADMAC and xyloglucan were approximately 0.2 mg/m^2 and 0.4 mg/m^2, respectively. The total increase of mass on the NFC model surface upon xyloglucan adsorption, derived from the QCM-D data by Eq. 1, was around 2.5 mg/m^2. Note that the values were determined at the 30 min mark for better comparison between the two methods. From the dry and the total adsorbed mass one may estimate that the water content of the adsorbed layer of xyloglucan was ~80%. Unfortunately, it was not possible to derive the corresponding values for PDADMAC or CMC from the experiments. However, it can be speculated that the adsorbed layer of CMC would have even higher water content due to its charged groups and loose adsorption conformation, and that the adsorbed layer of PDADMAC would have substantially lower water content due to formation of a flat and rigid adsorbed layer.

The QCM-D and SPR are good complementary techniques when it is possible to use the same model surfaces and adsorbates in similar experimental conditions. The techniques in parallel result in a powerful combination that is able to provide

information on the interdependence of interactions among the polymer, the solvent, and the surface.

In addition to the QCM-D and SPR studies, the aggregating/dispersing effects of xyloglucan, CMC, and PDADMAC on a native NFC suspension were assessed by confocal laser scanning microscopy (CLSM). Xyloglucan clearly dispersed the aggregated nanofibril suspension and reduced the average aggregate size to ~20 μm in contrast to the reference (~180 μm), while the effects of CMC and PDADMAC additions on the average aggregate sizes were rather small (see Paper II, CLSM images). The dispersing effect of xyloglucan was expected because it has been observed for fibre suspensions (Yan et al. 2006). As mentioned earlier (Chapter 4.1.1), the dispersing effect of CMC on the NFC suspension depends on the method of adsorption of the polymer; the adsorption of CMC at the specified conditions (Fig. 14c) was notably more effective in dispersing the fibril suspension as a comparison to plain addition of the polymer (see Paper II, CLSM image 4d). Similar behaviour has been observed in fibre suspensions after different CMC treatments (Liimatainen et al. 2009). The inability of PDADMAC to aggregate the fibril suspension was somewhat unexpected because another cationic polyelectrolyte, C-PAM, strongly aggregated the suspension (Fig. 14b). However, the charge density and the molecular weight of the polymers are quite different from each other. Plausibly, the highly charged, lower molecular weight PDADMAC was not able to induce bridging flocculation in the already aggregated NFC suspension, as proposed for C-PAM. It seemed that PDADMAC, during adsorption and mixing, was able to reverse the charge of the particles in suspension (at least partially), and thereby cause the generation of small particles among the larger aggregates (see Paper II, CLSM image 4c). Moreover, the observed behaviour is in accordance with flocculation mechanisms in fibre suspensions and the differences between C-PAM and PDADMAC have been observed also by AFM technique (Salmi 2009).

The interpretation of the microscopic level interactions as dispersing and aggregating effects of polymers on the NFC suspension can also be applied in explaining the molecular level phenomena in the QCM-D and SPR adsorption experiments. This interpretation is not exclusive to the discussion above but rather a suggestive complement to the interpretation of the results. The decrease in frequency and

increase in dissipation (Fig. 17) upon adsorption of xyloglucan could also mean that the polymer is able to disperse the cellulose nanofibrils, thereby increasing the water content and the viscous behaviour of the nanofibril/polymer layer. This would suggest that the xyloglucan is able to decrease the interaction between individual nanofibrils. It has been shown that xyloglucan forms a very thin (molecular) adsorbed layer on cellulose nanocrystals (Jean et al. 2009). Therefore, the observed changes could be partly accounted for the increased dispersion of the fibrils by xyloglucan (due to steric stabilization). It would also suggest that the polymer adsorption would affect the water binding of the nanofibrils *per se*, meaning that adsorption, swelling, and hydration would be interdependent, and thus would further complicate the interpretation of the adsorption data. By the same token, the QCM-D response to the adsorption of PDADMAC on the nanofibrils could be interpreted as aggregation or collapse of the entangled nanofibril network upon deswelling as a result of charge neutralization.

The studies on the interactions between polymers and cellulose fibrils clearly showed that different polymers interact in a different way with cellulose fibrils and, hence, have a different effects on the molecular-, micro-, and macro-scale behaviour of fibrous cellulosic materials. Many novel applications of cellulose fibrils and crystals in materials science, composites in particular, require stable and well dispersed starting materials. By careful consideration of the application and the interactions present, the adsorption of different polymers by electrostatic or specific interactions can provide a rather easy control over stabilization, compatibilization, and water affinity of the cellulosic material, in contrast to more laborious modification techniques, such as derivatization (Heinze & Liebert 2001; Lindström & Wågberg 2002).

4.2 Development of paper properties during drying

The working hypothesis of this thesis was that the addition of polymers into fibre suspension creates a gel-like fibre bonding domain that consists of fibre surface fibrils and adsorbed polymers. It was proposed that fibre bonding, wet web properties, strength development, and final sheet properties are influenced by the molecular level

interactions between cellulose and the polymers. As already shown (Chapter 4.1), the aggregation tendency and interaction with water of the cellulose fibrils are affected differently by dispersing or aggregating polymers. The properties of the fibre bonding domain depend on the molecular level interactions among cellulose fibrils, polymers, and water, as demonstrated by the adsorption experiments on model surfaces (Paper II).

As a part of Paper I, the development of tensile strength with certain polymers, i.e. CS, CMC, and chitosan, as a function of sheet dry solids was demonstrated. The method applied (Chapter 3.2.2) was an efficient and illustrative way to study the change of sheet properties upon drying. As shown by Mesic (2002) (Fig. 10), we also concluded that the strength development was very specific for different polymers and adsorption conditions (see Paper I, Fig. 5). In Paper III the method was applied to study the effects of guar gum, xyloglucan, chitosan, and CMC on the development of sheet tensile properties and drying tension. The selected polymers are known to have specific interactions with cellulose that enable adsorption in the absence of electrostatic interactions. A common dry-strength additive, CS, was included for comparison. The objective of Paper III was to "scale up" the molecular level interactions (adsorption studies on model surfaces) and the microscopically observed interactions (fibril dispersion or aggregation) to the macroscopic level of paper sheets.

4.2.1 The effect of polymers on the development of tensile properties

Obviously, the effect of a polymer as a strength additive depends on the amount adsorbed. However, the development of strength can be qualitatively very different between polymers (Paper I, Fig. 5), and thus the strength development can be assessed in spite of different adsorbed amounts of the polymers. Because the adsorption behaviour of the applied polymers was diverse (cationic, neutral, and anionic polymers) the adsorption conditions were carefully selected for each polymer, but compromises were required especially with the slowly adsorbing neutral polymers, guar gum and xyloglucan (for details, see Materials and Methods section in Paper III). Table 1 collects the adsorbed amounts of the applied polysaccharides on cellulose fibres.

Table 1. *Adsorbed amounts of polymers. (Paper III)*

Sample	Polymer addition [mg/g dry fibre]	Adsorbed amount [mg/g dry fibre]	Adsorption efficiency [%]
Guar gum	20	2.3 [a]	12
Xyloglucan	20	9 [a]	45
Chitosan 5-10 *	10	3.8 [b]	38
Chitosan 10-10 *	10	9.4 [b]	94
Chitosan 10-20 *	20	18.8 [b]	94
Cationic starch	15	9.6 [a]	64
CMC	20	15.4 [c]	77
CMC-chitosan bilayer	20+20	15.4 [c]+20 [b]	77 / 100

*) markings stand for adsorption pH and added amount of polymer, respectively.
a) acid-phenol test
b) polyelectrolyte titration at pH 5
c) conductometric titration

The adsorption efficiencies of the polymers are similar to those reported in literature (Christiernin et al. 2003; Laine et al. 2000; Laleg & Pikulik 1991), with the exception of guar gum for which the measured value of 12% was clearly lower in comparison to the reported values (Hannuksela et al. 2002). The difference was probably due to the higher beating level, presence of fines, and longer adsorption time in the work by Hannuksela et al. (2002). In regard to the adsorption experiments, it needs to be emphasized that the fibre preprocessing was optimized for the polymer adsorptions (for details, see Materials and Methods section in Paper III).

The experimental setup for measuring the development of paper strength during drying (Fig. 11) enabled collection of a large amount of stress-strain data at different sheet dry solids. Thus, a considerable amount of information on the rheological behaviour of paper sheets subjected to drying was obtained. Figure 19 exemplifies the remarkable change in stress-strain behaviour of certain samples as the sheet dry solids increased from 70% to 90%.

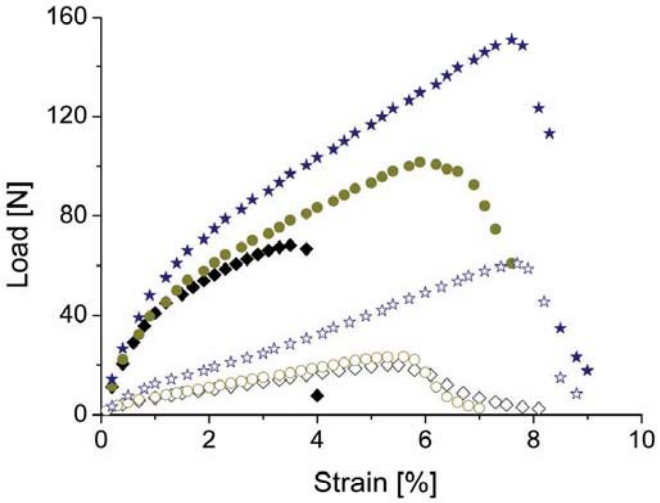

Figure 19. *Stress-strain curves of reference (♦), CS (●), and CMC-chitosan bilayer (★) samples at 70% solids (open symbols) and at 90% solids (filled symbols). (Paper III)*

As seen in Figure 19, CS did not affect sheet strength at 70% solids in the sheet. On the other hand, the enhancement in tensile strength, breaking strain, and modulus are obvious for the CMC-chitosan bilayer sample at both solids levels. The curves were selected to illustrate how the polymers influence the viscoelastic behaviour of paper upon drying. Hence, the following results of the development of sheet tensile properties are just a manifestation of this behaviour. The effect of different polymers on the development of tensile strength of wet pressed sheets through the drying range are presented in Figures 20-22. For clarity, the strength development curves as a function of sheet dry matter content are presented as the following three groups of polymers: 1) CS, guar gum, and xyloglucan samples; 2) chitosan samples; and 3) CMC containing samples. The figure insets magnify the low solids region of the plots.

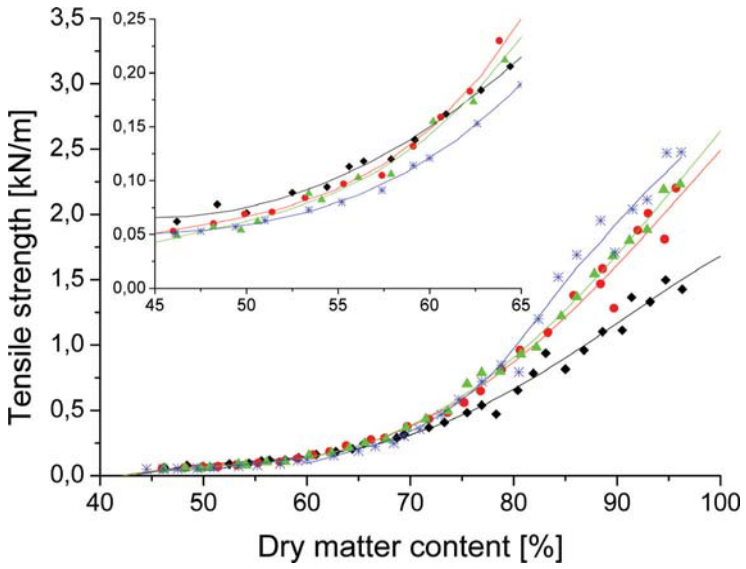

Figure 20. *Tensile strength development during drying of reference (♦) sheets and CS (✳), guar (●), and xyloglucan (▲) treated sheets. (Paper III)*

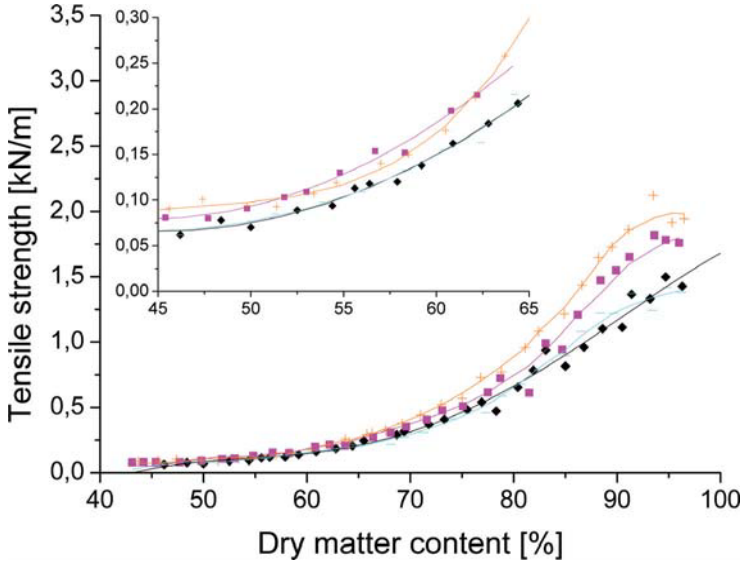

Figure 21. *Tensile strength development of chitosan samples under different adsorption conditions: 10 mg at pH 5 (–), 10 mg at pH 10 (■), and 20 mg at pH 10 (+). Reference (♦). (Paper III)*

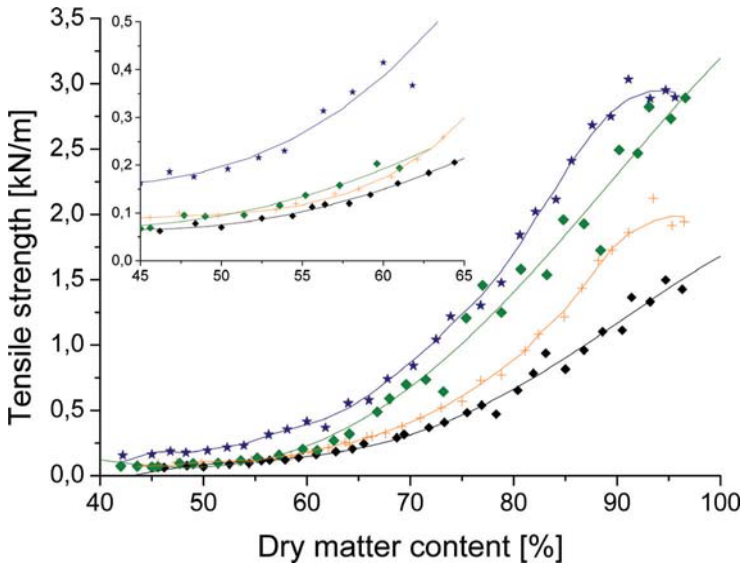

Figure 22. *Tensile strength development of CMC (♦) and CMC-chitosan bilayer (★) samples. Chitosan sample 20 mg at pH 10 (+) is included for comparison. Reference (♦). (Paper III)*

The effect of different polymers on the development of sheet tensile strength during drying was evident and depended on the applied polymer itself as well as on the adsorption conditions (Figs. 20-22). In more detail, guar gum and xyloglucan start to affect strength development at solids above 65%, whereas CS begins to increase the sheet strength at solids above 75%, in comparison to the reference. In addition, CS clearly decreased the wet web strength at solids below 65% (Fig. 20). The adsorption conditions are crucial for the effect of chitosan as a strength additive; when chitosan was adsorbed onto fibres at pH 5, it did not affect sheet strength at all, but when adsorbed at pH 10, both the wet web strength and the dry strength were improved (Fig. 21). The most prominent strength effects were achieved by CMC and the CMC-chitosan bilayer adsorptions (Fig. 22). CMC began to improve the strength noticeably at solids around 55%. The CMC-chitosan bilayer sample demonstrated superior wet web strength and strength development throughout the drying range (Fig. 22).

On the basis of the adsorbed amounts (Table 1), guar gum showed good potential in improving tensile strength. The development of tensile strength with 2.3 mg/g of adsorbed guar gum was similar to xyloglucan (9 mg/g), and only slightly lower when compared to cationic starch (9.6 mg/g), see Fig. 20. The strength potential of guar gum was not surprising since the good strength response of certain vegetable gums

has been known in papermaking for a long time. It has been connected to the high molecular weight and to the dispersing action of the polymers (Swanson 1950). However, CS is the most utilized strength additive due to the abundance and cheapness of the raw material, in contrast to, e.g., guar, karaya, or locust bean gums (Reynolds 1980).

Here, CS was used as a benchmark to which the other polymers could be compared. CS is advantageous in regard to dry strength, retention, and bonding (Reynolds 1980). However, the good dry strength properties come at the expense of wet web strength. As seen in Fig. 20 (also Paper I, Fig. 5), the wet web strength was impaired by CS and the strength was improved only above solids around 80%. The impairment of wet web strength by CS has been reported earlier (Laleg & Pikulik 1993). Plausibly, the wet web strength is influenced by the viscoelastic properties of the fibre bonding domain. The deswelling of fibrils and fibres by a cationic polymer (Paper II; Swerin et al. 1990) may partly influence the wet web strength by reducing the molecular level mixing and plasticization in the fibre bonding domain. On the other hand, it has been suggested that CS is adsorbed as clusters onto the fibre surface (Shirazi et al. 2003). Thus, the structure of the adsorbed layer may become diffuse and the cohesive strength of the fibre bonding domain in wet conditions would therefore be weaker.

CMC is excellent as a dry strength additive (Blomstedt et al. 2007; Laine et al. 2002) and it also improves sheet formation (Liimatainen et al. 2009; Yan et al. 2006). As shown above (Chapter 4.1, Papers I and II) CMC, when adsorbed at certain conditions, is able to disperse cellulose fibril suspensions as well as the fibrils on the fibre surfaces. CMC binds water onto the fibre surfaces, especially in the Na-counterion form (Berthold et al. 1994; Laine et al. 2002). The ability of CMC to disperse cellulose fibrils and to increase the hydration of fibre surfaces (or plasticization) promotes fibre bonding. Increased plasticization should improve the molecular level mixing in the fibre bonding domain and fibre bonding as well, in accordance with the theory of diffusion adhesion (Voyutskii 1963). The increased plasticization may also facilitate molecular level orientation as drying tension begins to exert strain on the sheet. Therefore, the increased strength and modulus by CMC could partly derive from the molecular orientation of the plasticized fibre bonding

domains during drying, as discussed earlier by Salmén et al. (1987) in the context of paper viscoelasticity.

Besides CMC, xyloglucan was found to have a clear dispersing effect on cellulose fibrils, though not as prominent as with CMC (Chapter 4.1, Papers I and II). The strength effect of xyloglucan was not as outstanding as that of CMC (Figs. 20 and 22). Possibly, xyloglucan improved the strength development by dispersing the fibre surface fibrillation in a similar manner as CMC. However, xyloglucan was less efficient because it was not charged and it bound less water to the fibre surface, compared to CMC. Xyloglucan has been proposed to create crosslinks between cellulose fibrils in the developing wood cell wall (Chanliaud et al. 2002; Whitney et al. 2006), and it has been found to affect the friction and adhesion properties of cellulose model surfaces (Stiernstedt et al. 2006). Both phenomena may partially influence the development of strength in the presence of xyloglucan.

Chitosan improves wet web strength but only when applied at elevated pH (Laleg & Pikulik 1991). Covalent bonding between chitosan and cellulose was suggested as a mechanism for improvement of wet web strength by chitosan (Laleg & Pikulik 1992), but direct evidence on covalent bonding between chitosan and cellulose at fibre surfaces was not shown. In another context, it was shown that chitosan reacted with cellulose fibrils and oligosaccharides via a rearrangement reaction, or carbonyl-amine condensation (Hosokawa et al. 1991; Umemura & Kawai 2007; Urreaga & de la Orden 2006). However, tracing the reacted structures or reaction products from the fibre surfaces at the concentrations present after chitosan adsorption would be challenging. Work by DiFlavio et al. (2005) on the wet strength mechanism of another polyamine, polyvinylamine (PVAm), emphasized the contribution of covalent bonding to the wet adhesion between cellulose and PVAm, but also bonding by electrostatic attraction was considered significant. The levelling off of the strength in chitosan containing samples at solids above 90% (Figs. 21 and 22) could originate from chemical crosslinking, known to cause brittleness in paper sheets (Espy 1995). The chemical crosslinking mechanism is also supported by the increased strength of rewetted paper sheets treated with chitosan (Allan et al. 1978), which is normally achieved with reactive wet strength additives (Espy 1995; Wågberg & Björklund 1993). On the other hand, the viscoelastic and adhesive properties of the adsorbed

chitosan layer may have a crucial influence. At high pH, where chitosan becomes insoluble, a phase transition in the fibre surface layer is expected. If the phase transition increases the adhesion between adsorbed chitosan layers on the fibre surfaces, the wet web strength should improve. Recently, studies on the origin of wet web strength suggested that entanglement friction was an essential factor for wet web strength, in particular, above the fibre saturation point, i.e. at solids where free water was not anymore present in the wet web (de Oliveira et al. 2008; van de Ven 2008). Since chitosan improves the wet web strength, it was considered beneficial to study if chitosan adsorption indeed has an effect on the viscoelastic and adhesive properties of fibre surfaces. This was realized in Paper V by using the QCM-D and AFM techniques on model systems.

Surprisingly, it was possible to combine the beneficial effects of CMC on strength development at solids above 50% with the capability of chitosan to improve wet web strength at low solids by controlled bilayer adsorption. In particular, the initial wet strength and wet strength at low solids were remarkably higher with the CMC-chitosan bilayer sample compared to other samples (Fig. 22). Since the chitosan adsorption was performed at elevated pH, the term “bilayer adsorption” may be misleading as we can not at this point prove that the structure of the adsorbed layer was, indeed, a bilayer. It was rather assumed that the fibre bonding domain was a mixed layer of colloidal chitosan particles and CMC stabilized fibre surface fibrils, and that the viscoelastic properties of such a bonding domain influenced the development of strength upon drying. Generally, very good strength properties can be attained by multilayer adsorption of polyelectrolytes onto fibres (Ankerfors et al. 2009; Wågberg et al. 2002). However, here the emphasis was on polysaccharides that are substantive to cellulose by other than electrostatic attraction.

Adsorption of chitosan at pH 5 did not affect strength development (Fig. 21), which contradicted the results from literature showing that chitosan improved dry strength at low pH (Allan et al. 1978; Lertsutthiwong et al. 2002). Possibly, the adsorbed amount of chitosan (3,8 mg/g, Table 1) was not high enough for a polymer of molecular weight around 400 kg/mol to influence bonding in the absence of fines. Indeed, in previous studies the fines had not been removed, which may have increased the adsorbed amount of chitosan to levels that showed an increase in strength.

In addition to tensile strength, the breaking strain is an important characteristic of paper. The change in breaking strain with different polymers as a function of sheet dry matter content is presented in Figure 23. The results are presented in the same groups of polymers as before (Figs. 20-22).

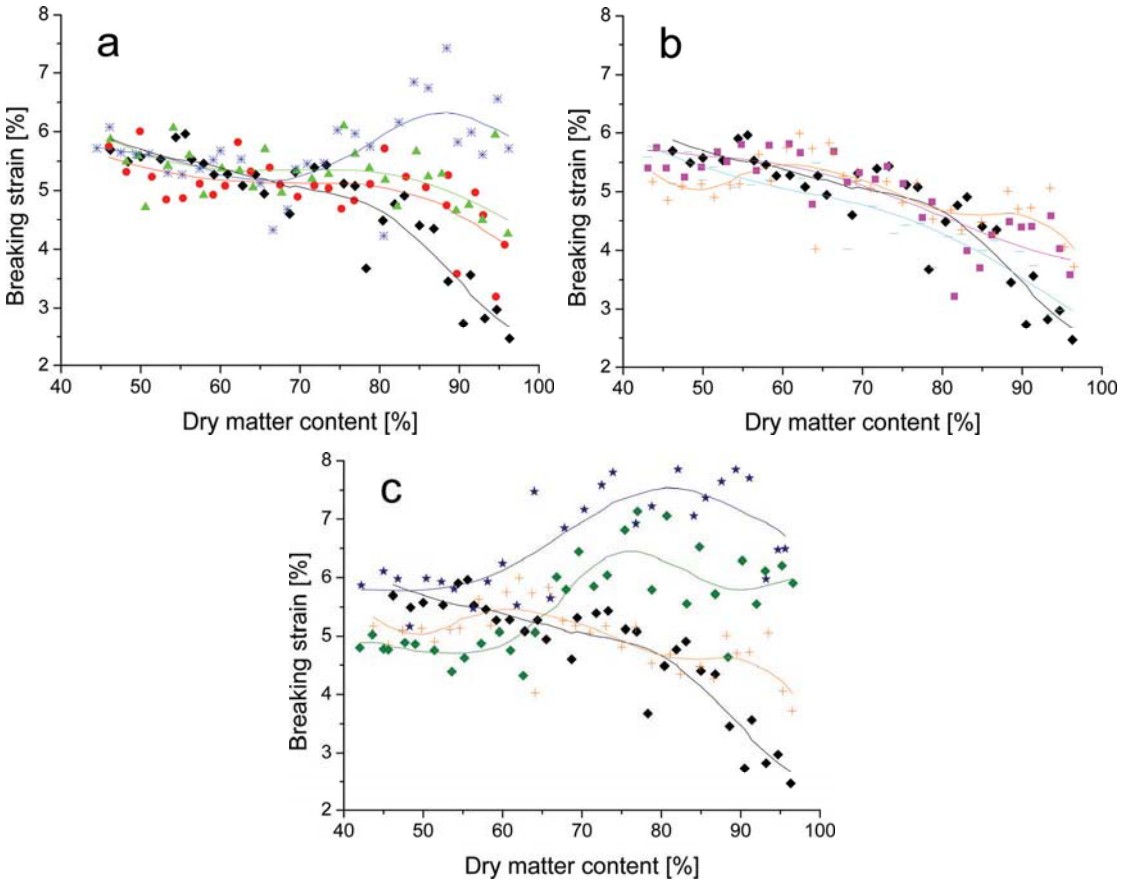

Figure 23. a) *Change of breaking strain during drying of reference (♦) sheets and CS (✳), guar (●), and xyloglucan (▲) treated sheets.* ***b)*** *Chitosan samples at different adsorption conditions: 10 mg at pH 5 (–), 10 mg at pH 10 (■), and 20 mg at pH 10 (+).* ***c)*** *CMC (♦) and CMC-chitosan bilayer (★) samples, chitosan sample 20 mg at pH 10 (+) is included for comparison. (Paper III)*

As seen from the reference curve, the breaking strain of paper generally decreases upon drying; it decreased from ~5.5% strain of a wet sheet to ~2.5% strain of a dry paper in the absence of polymer additives. However, the effects of different polymers on the breaking strain can be remarkable. At solids above 70% CS, xyloglucan, and guar gum increased breaking strain in comparison to reference, CS being the most efficient (Fig. 23a). Interestingly, chitosan had only a minor influence on the breaking strain at any adsorption condition (Fig. 23b). In contrast, the most remarkable

increases in breaking strain were attained with CMC and the CMC-chitosan bilayer adsorptions at solids above 60-70%. Especially the CMC-chitosan bilayer sample demonstrated high breaking strain values throughout the drying range (Fig. 23c).

The development of breaking strain between polymers was different (Figs. 23a-c), on a qualitative basis, in comparison to the development of tensile strength (Figs. 20-22), suggesting that the mechanisms affecting these properties may be different. As shown in Fig. 23c, CMC was the only polymer that clearly decreased breaking strain at low solids (<65%). The decrease in breaking strain by CMC can be related to the decreased friction between fibres after CMC adsorption (Horvath & Lindström 2007; Zauscher & Klingenberg 2001). Moreover, the decrease in breaking strain by CMC at low solids, i.e. at solids where free water was still present in the wet web, is in accordance with the aforementioned crucial role of entanglement friction in the wet web strength of paper (de Oliveira et al. 2008; van de Ven 2008). Even though chitosan did not much affect the breaking strain when adsorbed onto plain fibres, it clearly increased the breaking strain of the CMC treated fibres in the case of the CMC-chitosan bilayer sample (Fig. 23c). The mechanism of action of chitosan is hardly resolved, but it seemed that after CMC adsorption the interaction between the fibre surface and the precipitated chitosan was much more pronounced than between chitosan and the reference fibre surface, even though the adsorbed amount of chitosan was approximately the same.

Other tensile properties derived from the measured stress-strain data included tensile energy absorption (TEA) and modulus. Expectedly, the effects of polymers on the TEA were quite pronounced at high solids because the polymers improved both the tensile strength and breaking strain. For example, the TEA values of reference and CMC-chitosan bilayer samples at 90% solids were 20 J/m^2 and 140 J/m^2, respectively, showing a 7-fold increase in the TEA while the tensile strength and breaking strain were approximately doubled. The sheet modulus was only affected at high solids (>75%). CMC adsorption was found to improve the modulus the most, whereas CS did not influence the modulus appreciably in spite of considerable improvement in strength. The tensile stiffness of CMC treated sheets can be influenced by application of drying restraints (Blomstedt et al. 2007). Similarly, the drying tension developed upon drying may affect the modulus.

4.2.2 Development of drying tension

The development of drying tension was measured with the same experimental setup as the strength development. The drying tension was measured as the tension developed upon drying under longitudinal restraints, i.e. the tension was not allowed to relax between the points of measurement. Figures 24a-c show the development of drying tension for the different polymer treated sheets as a function of dry matter content in a range of 65-95%. The results are presented in the same groups of polymers as before.

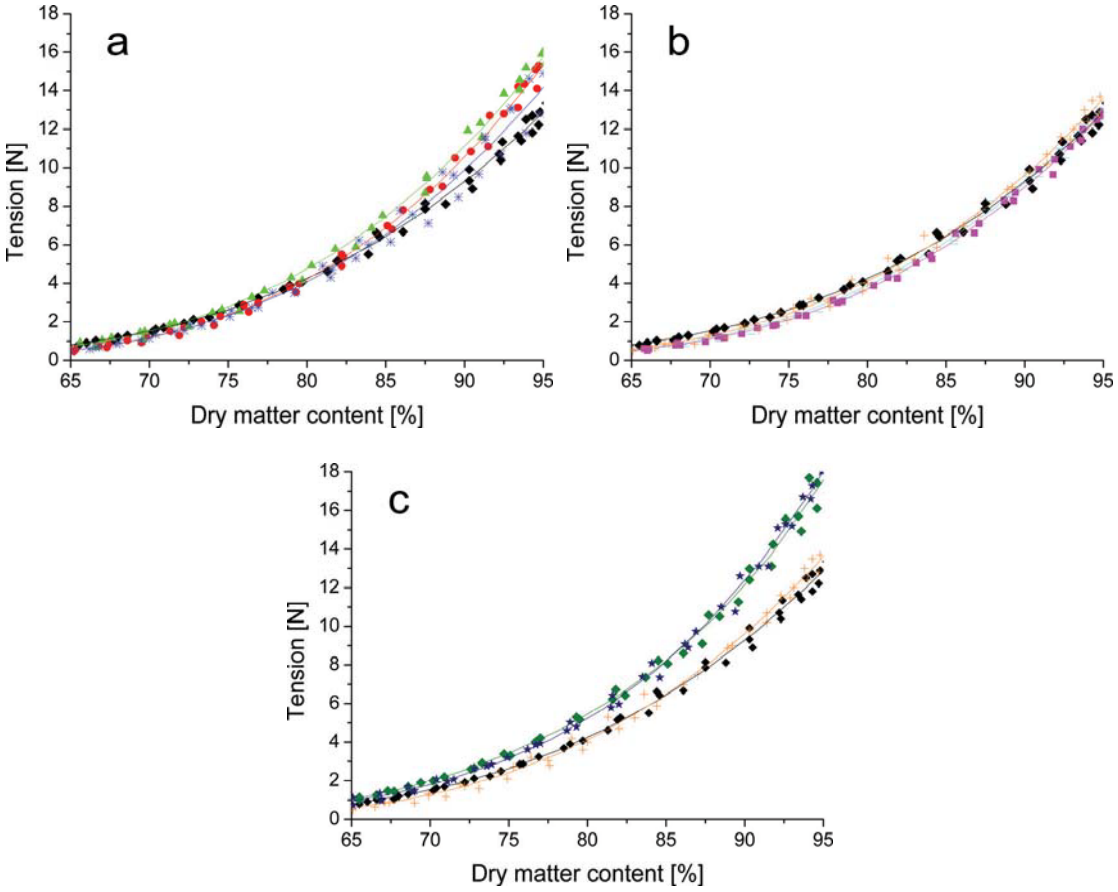

Figure 24. a) *Development of drying tension as a function of sheet dry matter content of reference (♦) and CS (✳), guar (●), and xyloglucan (▲) treated sheets.* ***b)*** *chitosan samples at different adsorption conditions: 10 mg at pH 5 (–), 10 mg at pH 10 (■), and 20 mg at pH 10 (+).* ***c)*** *CMC (♦) and CMC-chitosan bilayer (★) samples, chitosan sample 20 mg at pH 10 (+) is included for comparison. (Paper III)*

As seen in Figure 24a, xyloglucan somewhat increased the drying tension at high solids, whereas the effects of CS and guar gum were rather insignificant. CMC adsorption increased the drying tension the most (Fig. 24c). Conversely, chitosan, irrespective of adsorption conditions, had no influence on drying tension, even in the case of CMC-chitosan bilayer adsorption (Figs. 24b-c).

The development of drying tension was quite different from the other results. The shrinkage force in paper mainly originates from the lateral shrinkage of the fibres which is transferred through fibre bonds to the paper structure (Wahlström & Fellers 2000). It seemed that the drying tension mainly derived from the swelling and shrinkage tendency of the bulk fibre material but the adsorbed polymers influenced the drying tension as well (Fig. 24). Plausibly, the adsorption of CMC dispersed the fibrils on the fibre surfaces and increased the swelling of the surfaces, which then further improved bonding through plasticization and molecular level mixing in the fibre bonding domain. The increased drying tension by CMC adsorption can be partly accounted for the enhanced fibre bonding. The effect of xyloglucan can probably be paralleled to the dispersive action of CMC, though xyloglucan was less efficient in dispersing cellulose fibril suspensions. Since the fibre material, and therefore the fibre wall too, was the same for all samples, the increased drying tension by xyloglucan and CMC is proposed to be a consequence of the increased dispersion and swelling of the fibre surface fibrils. If the increased drying tension was accounted for solely on the improved fibre bonding, the lack of any influence of chitosan on the development of drying tension would be difficult to explain, because chitosan affected strength development already at low solids. This implies that improved bonding by the polymers (CMC and xyloglucan) is not a satisfactory explanation for the increase of drying tension, but another factor, proposedly the increased swelling of the fibre surface, is also operational. In general, the development of drying tension and its mechanisms in the presence of different polymers still remain somewhat uncertain.

4.3 Water plasticization in polymer-cellulose composites and paper

Composite materials containing cellulose have been of interest due to their environmentally friendly origin and high specific strength (Samir et al. 2005; Berglund 2005; Dufresne 2006; Hubbe et al. 2008; Kohler & Nebel 2006; Kramer et al. 2006; Zimmerman et al. 2004). In this thesis, composite films made of cellulose fibrils and polymers were used as a model of material in the fibre bonding domain in dry paper. It was expected that the mechanical behaviour of the composites would provide information on the compatibility and on the interactions among the components as well as on the nature of fibre bonding in the presence of strength additives. The preparation of composite films and their properties were shortly introduced in Paper I**,** see Chapter 4.1.1 (Fig. 16). The influence of moisture plasticization of polysaccharides on the properties of composite films and paper sheets was indirectly evidenced already at the early stages of this thesis work. Thus, a more detailed study on the moisture plasticization of cellulose-polymer composites and paper was included (Paper IV).

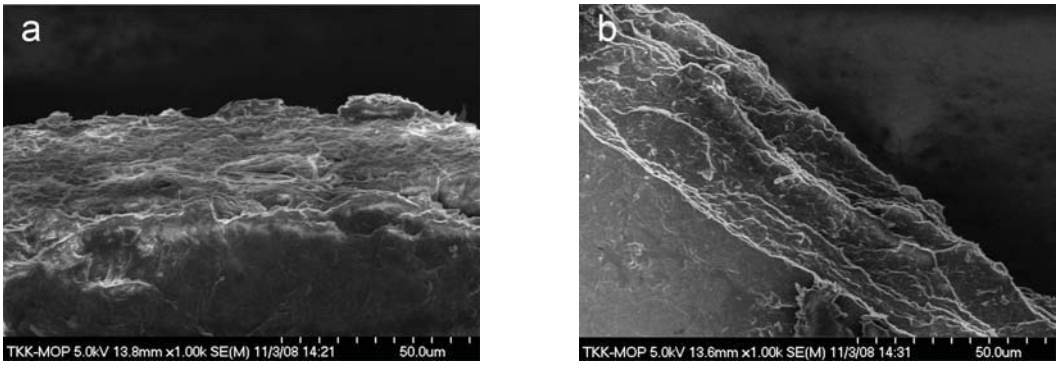

Figure 25. *SEM images of cryo-fractured surfaces of* ***a****) MFC film and* ***b****) MFC-CMC (32 wt-%) composite film. (Paper IV)*

When fibrillar cellulose is moulded to a composite film, by casting and evaporation or by other methods, a lamellar film structure is obtained (Fig. 25a). This type of structure has been found in several studies where the cellulose has been the main component (Dammström et al. 2005; Henriksson 2008; Svagan et al. 2007). The incorporation of polymer (32 wt-% of CMC) reduced the porosity of the composite film (Fig. 25b). Porosity or density is crucial for the ultimate strength properties of

composites. Here a non-destructive mechanical testing method was used and relative modulus values were calculated in order to ensure the comparability between samples regardless of slight differences in sample densities.

Figure 26 shows the moisture plasticization of MFC composite films with (a) CMC and (b) chitosan at polymer content of 10% and 20% in comparison to the MFC reference film. At low polymer content neither guar gum nor xyloglucan had an appreciable effect on the plasticization of the composite films (data not shown). However, CMC, especially at 20% polymer content, increased the plasticization in the composite at relative humidity (R.H.) above 60% (Fig. 26a). Conversely, chitosan seemed to hinder the film plasticization at high R.H. levels (Fig. 26b).

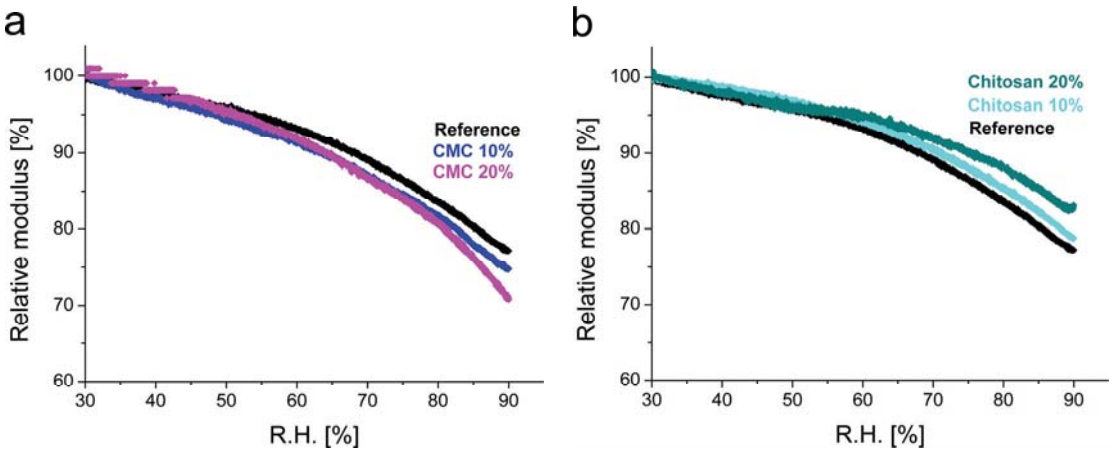

Figure 26. *Plasticization of* ***a****) CMC containing and* ***b****) chitosan containing (10 and 20 wt-%) MFC composites as a function of relative humidity. (Paper IV)*

Films of cellulose fibrils demonstrate high strength and modulus (Henriksson 2008; Nakagaito & Yano 2005; Nakagaito et al. 2005; Svagan et al. 2007). Also here, the continuous MFC phase dominated the viscoelastic and sorption properties of the composites. Thus, the effect of polymers at low additions was not that pronounced. However, it has been shown that if a polysaccharide is intimately associated with cellulose fibrils its effect on moisture plasticization may be masked (Dammström et al. 2009). On this ground, the inability of xyloglucan, which is known to closely associate with cellulose (Jean et al. 2009), to influence the plasticization is also explicable, but it would require further studies on xyloglucan-cellulose composites to verify this speculation.

In order to make the effects of polymers on the moisture plasticization of the films more discernible, the polymer content of composites was increased to 32 wt-%. Figure 27 shows the effect (a) of CMC and (b) of chitosan and cationic starch at a content of 32 wt-% on the plasticization of the composite films in comparison to the reference MFC film. Again, xyloglucan and guar gum did not have an appreciable effect on the plasticization (data not shown). CMC plasticized the composite at R.H. above 65% (Fig. 27a), whereas chitosan and CS had the opposite effect on plasticization (Fig. 27b).

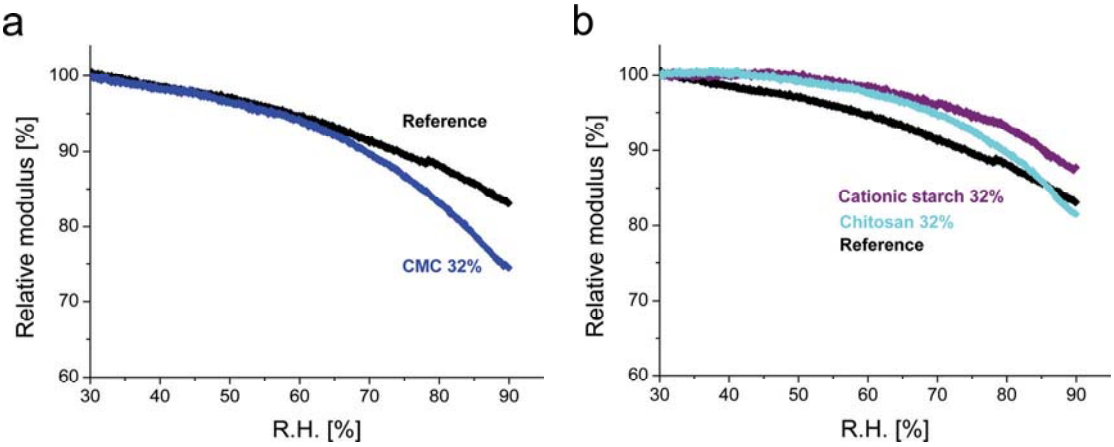

Figure 27. *Plasticization of* ***a)*** *CMC and* ***b)*** *CS and chitosan containing (32 wt-%) MFC composite as a function of relative humidity. (Paper IV)*

The ability of chitosan and CS to hinder the moisture plasticization may suggest that the electrostatic interactions are of importance in regard to the plasticization behaviour. The charge of the MFC is slightly anionic due to presence of carboxylic groups. In addition, the sodium counter-ion form of lignocellulosic materials is the most sensitive to moisture (Berthold et al. 1994; Hatakeyama et al. 1995). Hence, it was expected that the polymers would change the absorbed moisture content of the composites and by that way would affect the overall plasticization of the composites. The moisture sorption of the composite films was determined with TG after equilibration of the composites at different R.H conditions. The measured equilibrium moisture contents (emc) at different R.H. levels showed rather high scatter due to the measurement technique. However, the high ability of CMC to increase the plasticization at high R.H. levels was explained by the results. The emc of the composite film with 32% CMC content was ~13%, whereas the emc of the MFC

reference film was ~11%, at relative humidity level of 85% (see Paper IV, Table 1). On the contrary, the hindered plasticization by chitosan or CS was not detected as a decrease in the emc by the polymers, at least not within the precision of the measurement method.

It was proposed that the composite properties could describe the behaviour of fibre bonding domain in the presence of paper strength additives (Paper I). In order to compare the plasticization of paper and the composites, a set of paper samples prepared in the previous study (Paper III) were measured with the DMA. The moisture plasticization of paper samples treated with CMC, chitosan, and both (CMC-chitosan bilayer sample) was measured by DMA similarly as the composite films (Fig. 28). Evidently, the plasticization behaviour of the paper samples was dominated by the bulk fibres but the different polymer treatments influenced the plasticization to some extent. Unexpectedly, the CMC treated paper was the most resistant towards plasticization while the plasticization behaviour of chitosan containing samples was closer to that of the reference sheet, in contrast to the plasticization of the composite films (Figs. 26-27). The plasticization of paper samples was somewhat more intense compared to the composite films, which indicates the strong dependence of fibre network bonds in the paper structure. Plausibly, in paper the influence of polymers on plasticization may be more indirect through bonding in the fibre network structure and through density effects.

In a study on the function of polyacrylamide as a strength additive, the effect of the polymer was found to be dependent on the mode of addition of the polymer (Mihara & Yamauchi 2008). It was shown that by impregnation, the polymer characteristics were observable in DMA, but after polymer adsorption onto fibres those features were not seen. The molecular level mixing of the polymer with the fibre surface on adsorption was proposed as a reason. In addition, as support to our working hypothesis, it was proposed that the adsorbed polymer forms a kind of composite structure with cellulose that improves bonding between fibres, i.e. increases bond strength per unit bonding area (Mihara & Yamauchi 2008). Another work, elaborating fibre bonding in more detail, differentiated between unit bonded area and unit bonding strength and the polymers were found to affect both, but especially the increase in unit

bond strength was clearly evident (Torgnysdotter 2006). This emphasizes the importance of molecular level phenomena in fibre bonding.

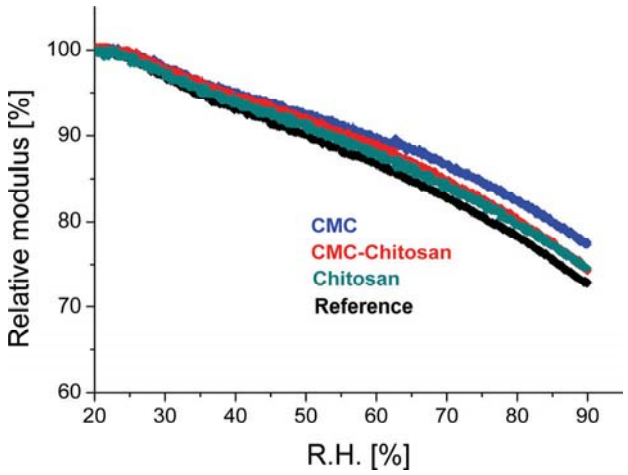

Figure 28. *Plasticization behavior of paper samples treated with chitosan, CMC, and CMC and chitosan consecutively (CMC-chitosan bilayer adsorption). (Paper IV)*

Overall, since polysaccharides are plasticized by water and the transitions, like glass transition temperature, are thereby influenced as well (Salmén & Olsson 1998; Stading et al. 2001), the measurement of strength, viscoelastic, and creep properties at defined conditions with regard to surrounding humidity, temperature, and moisture sorption can provide crucial information on the usability of the materials at given conditions. In comparison to thermoplastic polymers and composites, the plasticization of polysaccharides by water, and not as much by merely heat, requires that moisture is considered as the critical factor on the behaviour of these kinds of materials. Therefore, the R.H. controlled DMA along with other methods – IR spectroscopy (Dammström et al. 2005; Hofstetter et al. 2006), moisture sorption (Svagan et al. 2009), and creep measurements (Gimåker et al. 2007; Larsson & Wågberg 2008) – are very useful for reaching a thorough understanding of behaviour and structure-property relationships of polysaccharide containing materials.

4.4 Interactions between cellulose and chitosan

The peculiar adsorption behaviour of chitosan at different pH and the superior wet web strength obtained by chitosan (Papers I and III) justified a further examination of the specific interactions between cellulose and chitosan by the QCM-D and AFM techniques (Paper V). Special attention was paid to demonstrate the proposed specific non-electrostatic interactions between the polymers and to elucidate the mechanisms of action of chitosan as a wet web strength additive.

4.4.1 Effect of pH on the adsorption of chitosan

The adsorption of chitosan on an LS-cellulose model surface at different pH was studied by QCM-D. Figure 29a shows the QCM-D frequency and dissipation curves for chitosan adsorbed at pH 5 followed by subsequent pH increments in different buffer solutions. In the beginning, chitosan was adsorbed on the cellulose model surface at pH 5, then the unadsorbed polymer was rinsed off by buffer of the same pH. Thereafter, buffer solutions of increasing pH were applied to the surface. Changes in frequency (Δf) and dissipation (ΔD) were followed throughout the measurement. Figure 29b presents the QCM-D frequency and dissipation curves for chitosan adsorbed at pH 6.5 followed by subsequent pH increments. For comparison, a plain LS-cellulose surface without chitosan adsorption step was run through the same sequence of buffer solutions, shown in Figure 29c. A separate adsorption experiment of chitosan onto LS-cellulose surface at pH 2 is presented in Figure 29d.

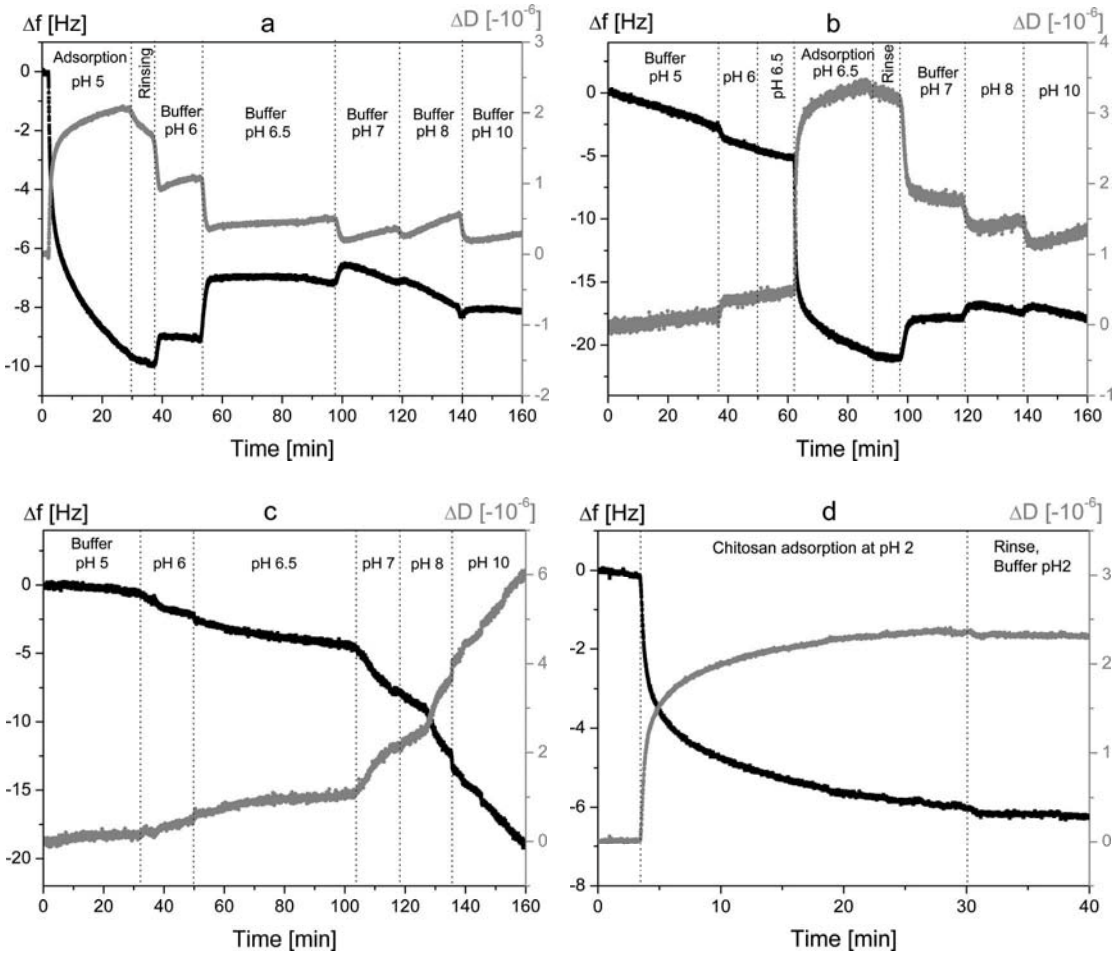

Figure 29. *QCM-D frequency and dissipation curves of chitosan adsorption and the influence of gradual increase of pH on the adsorbed layer;* ***a****) at pH 5,* ***b****) at pH 6.5,* ***c****) in the absence of chitosan, and* ***d****) at pH 2 (only adsorption experiment). (Paper V)*

Injection of the chitosan solution induced a clear decrease in the frequency and increase in dissipation. Subsequent rinsing did not affect the frequency but it decreased the dissipation, which indicated irreversible adsorption of chitosan on the cellulose surface. The subsequent changes in pH by different buffer solutions had a clear effect on the adsorbed polymer layer, as expected. When changing the pH from pH 5 to pH 6 (Fig. 29a, time ~40 min), a sharp increase in frequency and decrease in dissipation were observed. The same was observed on the change from pH 6 to pH 6.5 (Fig. 29a, time ~55 min). The changes in frequency and dissipation reflected changes in polymer conformation and in the amount of water associated with the chitosan/cellulose layer. The changes were found to be reversible with pH to a large extent, thus desorption of the chitosan was not the main reason for the observed behaviour. However, the desorption of chitosan to a small extent by the pH changes

could not be completely excluded because electrostatic interactions are present at pH 5 and pH 6.5. The gradual increase of pH from pH 5 to pH 6.5, in Fig. 29a, removed water from the polymer layer (increase in frequency) and made the layer more elastic (reduced dissipation). The adsorbed amount of chitosan increased with pH as the negative charge of cellulose was increased and positive charge of chitosan was decreased at the pH 6.5 (Fig. 29b). Because QCM-D senses the total mass increase on the sensor surface, the amount of associated water in the chitosan layer is an important factor. At above pH 6.5, where chitosan became insoluble, the decrease in frequency (or adsorbed amount) can be mainly associated with the exclusion of water from the polymer layer upon the phase change. The QCM-D results are in accordance with the observed chain extension of chitosan at low pH and collapsed conformation at higher pH (Nordgren et al. 2009).

The solubility limit of chitosan was around pH 6.8. The change in solubility was also indicated by the decrease in dissipation at above pH 6.5, suggesting a clear transition in the viscoelastic properties of the adsorbed chitosan layer (Figs. 29a,b). The change in viscoelasticity should reflect to the molecular level interactions between chitosan and cellulose. The strength development results (Paper III) suggested that the viscoelastic properties of the fibre bonding domain may influence the attained wet web strength by chitosan at a pH where the polymer is insoluble. Recently, friction between fibre surfaces was cited as an important factor for wet web strength of paper (de Oliveira et al. 2008; van de Ven 2008). The frictional properties of cellulose model systems in the presence of different polymers have been studied by the AFM colloidal probe technique in the immersed state (Nordgren et al. 2009; Zauscher & Klingenberg 2001). Also, the wet adhesion between cellulose model surfaces has been studied with the same technique (Notley et al. 2009).

Work by Nordgren et al. (2009) suggested that adsorption of chitosan onto cellulose involves an interaction of non-electrostatic nature. Indeed, the specific, non-electrostatic, interaction between cellulose and chitosan was evident in the QCM-D experiment (Fig. 29d). The LS-cellulose surface was virtually uncharged (carboxyl groups protonated) at pH 2, i.e. the experiment was done in the absence of electrostatic attractive interaction between cellulose and chitosan. However, the polymer still adsorbed to the cellulose surface. If only electrostatic attraction had been

the driving force of the adsorption, the cationic chitosan would not have been adsorbed onto the cellulose at pH 2. The mechanism of adsorption of certain linear 1-4-β-glucans on cellulose has been related to the structural similarity of the polymers (Hannuksela et al. 2002; Mishima et al. 1998; Zhou et al. 2007). The suggested covalent reactions between chitosan and cellulose (Hosokawa et al. 1991; Laleg & Pikulik 1992; Umemura & Kawai 2007; Urreaga & de la Orden 2006) may also affect the adsorption of chitosan.

The structure and morphology of the LS-cellulose model surfaces after the adsorption experiments with the QCM-D were studied by AFM imaging. Figure 30 shows AFM images of a) the reference LS-cellulose surface, b) LS-cellulose surfaces after chitosan adsorption at pH 5, and c) at pH 6.5.

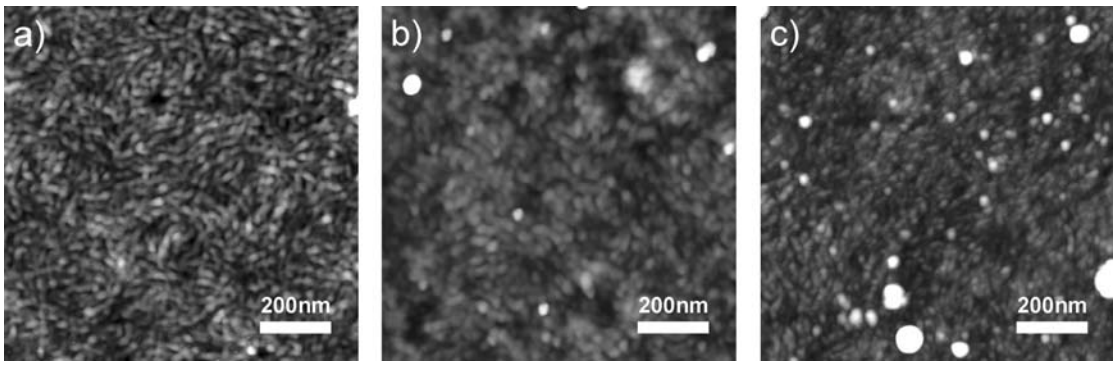

Figure 30. *AFM images of LS-cellulose surfaces after QCM-D adsorption experiments:* ***a****) reference,* ***b****) chitosan adsorbed at pH 5, and* ***c****) chitosan adsorbed at pH 6.5. (Paper V)*

It seemed that the adsorbed chitosan formed small round domains, observable by AFM, onto cellulose (Fig. 30b,c). It could be that the domains were chitosan in agglomerated form. Formation of chitosan agglomerates on a poly(ethylene terephtalate) surface at a pH above the solubility limit of the polymer has been previously observed by AFM (Indest et al. 2008). However, in this case, there was not such a significant differences between the samples in the occurrence of the round domains that they could be linked to presence of chitosan agglomerates for certain.

Seeing that the swelling of the LS-cellulose surface was restricted by chitosan adsorption (compare Figs. 29a and 29c), it is conceivable that a layer of adsorbed chitosan molecules has formed over the cellulose film, which could act as protective or constraining layer towards swelling when the chitosan is in the insoluble state. In addition, neutralization of the negative charge of cellulose by the cationic chitosan can reduce the swelling of cellulose. Moreover, the reduced swelling in the immersed state implies that the interactions between cellulose and water molecules are reduced, which could explain the decreased plasticization by moisture in the MFC-chitosan composites as well (Figs. 26b and 27b). The observed swelling behaviour could be related to the action of chitosan as wet strength agent for paper (Allan et al. 1978), since the decreased swelling of fibres has been proposed as a mechanism of permanent wet strength for polyamines, like PEI and PVAm (Linhart 2006).

4.4.2 Adhesion between chitosan and cellulose

The interfacial behaviour of the adsorbed chitosan layer on cellulose surfaces was studied in more detail by AFM colloidal probe experiments at similar conditions as the QCM-D measurements. The surface forces between a cellulose sphere and the LS-cellulose model surface upon approach were measured at different pH in the absence and presence of adsorbed chitosan. The surface force between the cellulose surfaces was repulsive and short-range prior to addition of chitosan (Fig. 31, reference). After chitosan adsorption at pH 5, a substantial increase in the magnitude and range of repulsion was observed (Fig. 31, filled squares). When the pH was increased to pH 6.5, the repulsion decreased clearly (Fig. 31, filled circles), indicating a collapse of the chitosan layer. This supported the observation from the QCM-D experiments that the chitosan layer excluded water as the solubility of chitosan decreased with pH. At higher pH (pH 7 to pH 10) the compressibility of the surface decreased and the separation between the surfaces became indeterminate, possibly due to swelling of cellulose. Hence, the surface forces at high pH are not presented. The influence of pH on the swelling of a cellulose surface have been presented e.g. by Ahola et al. (2008a).

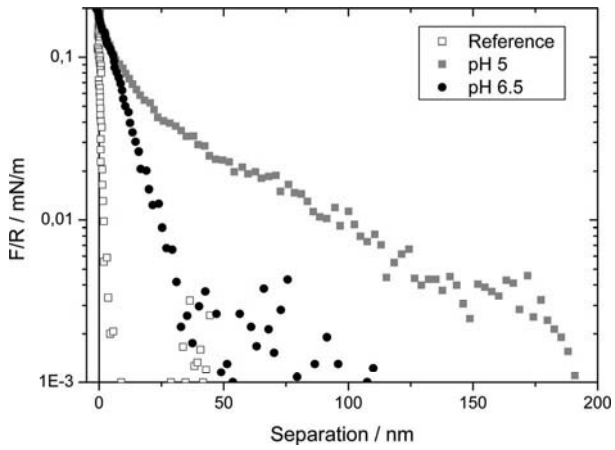

Figure 31. *Surface forces on approach between cellulose surfaces at different pH. Reference curve (open squares) is the surface force between cellulose surfaces (at pH 5) prior to chitosan addition. Filled symbols are for surface forces after chitosan adsorption. (Paper V)*

Table 2. *Maximum magnitude and range of the pull-off force between the chitosan coated cellulose surface as a function of pH and load. The reference is the pull-off force between pure cellulose surfaces prior to chitosan adsorption. (Paper V)*

Sample	Load [nN]	Pull-off force [mN/m]	Relative std. dev. [%]	Range [nm]
Reference	6.2	13	136	25-40
pH 5	10.4	24	54	100-400
pH 6.5	11.3	25	87	50-400
pH 7	10.6	61	61	200-850
pH 8	10.4	46	28	200-850
- " -	13.5	73	33	200-850
- " -	17.9	93	13	*
pH 10	9.0	20	52	150-450

*) the shape of the pull-off force curve changed

The adhesive properties of the chitosan/cellulose interface were evaluated from the pull-off force, i.e. from the force recorded upon retraction of the surfaces. The maximum values and ranges for the pull-off force at different pH and applied loads are collected into Table 2. Between plain cellulose surfaces the pull-off force was low and short-range. The pull-off force and its range increased slightly in the presence of adsorbed chitosan at pH 5 and pH 6.5, where chitosan was still in the water-soluble state. However, the pull-off force increased significantly and the range of the pull-off force was very long at pH 7 and pH 8. Evidently, the phase change of chitosan from soluble (pH 6.5) into insoluble (pH 7) influenced the pull-off adhesion. On separation

of the surfaces, the chitosan molecules gradually detached from the opposite surface causing the saw-tooth pattern observed in the pull-off force curve (exemplified in Figure 6). Interestingly, at pH 10 the observed pull-off force decreased to a similar level as in pH 5 and 6.5. This was probably caused by gradual swelling of cellulose at the high pH. However, this was in line with an observation during earlier experiments (Paper III) that the strong flocculation tendency of the chitosan treated fibre suspension reduced at elevated pH (~pH 10). It could be that the increased swelling of cellulose reduced the flocculation or that at high pH the adhesion or friction between chitosan coated cellulose surfaces was reduced.

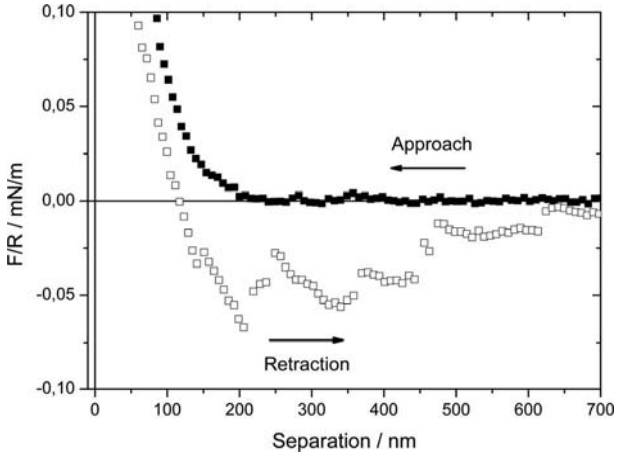

Figure 32. *Pull-off force (open symbols) between chitosan coated cellulose surfaces at pH 7. Filled symbols are for the data on approach. (Paper V)*

The results above emphasize the pH dependent adsorption and phase behaviour of chitosan as important factors regarding the wet web strength (and dry strength) of chitosan treated paper (Paper III; Laleg & Pikulik 1991; Lertsutthiwong et al. 2002). The increase of wet adhesion between chitosan coated cellulose surfaces at pH above the solubility limit can be related to the improvement of wet web strength of paper. Furthermore, since the adsorption behaviour of chitosan was similar to that of any polyelectrolyte at pH 5, where chitosan did not affect the wet web strength of paper, gives support to the interpretation. The phase transition near the solubility limit of the polymer is decisive for the action of chitosan as strength additive. However, it was not clarified whether the molecular level mechanism was chemical reactions and crosslinking (Hosokawa et al. 1991; Laleg & Pikulik 1992; Umemura & Kawai 2007; Urreaga & de la Orden 2006) or something else, like the increased tackiness of colloidal chitosan particles near the solubility limit (Hubbe et al. 2006).

5 CONCLUDING REMARKS

In this thesis work a new approach to fibre bonding, paper strength, and to the mechanism of action of different paper strength additives was applied. The interactions between the fibrillar structure of fibre surfaces and the adsorbed polymers were studied at the molecular and microscopic levels, and the implications of the interactions were assessed on a macroscopic level in paper sheets. The consideration of the fibre bonding domain as a gel-like structure consisting of hydrated cellulose fibrils and adsorbed polymers helped to connect the interactions between cellulose fibrils and polymers to the development of bonding and strength properties in fibre network.

The molecular level and microscopic studies on the interactions between cellulose fibrils and polymers showed that the polymer type and the adsorption conditions are decisive to the properties of the system. The inherent aggregation tendency of cellulose fibrils can be affected by dispersing or aggregating polymers, such as CMC and C-PAM. The dispersing and aggregating effects of polymers in a suspension of cellulose fibrils were virtually the same when compared to the observations from the fibrillated fibre surfaces. In addition, the hydration of the cellulose fibrils was affected by the polymers; a dispersing polymer increased the amount of associated water in the cellulose fibril/polymer layer whereas a cationic flocculant caused dehydration of the layer. The dispersing and aggregating effects, observed in the model systems, were further related to the viscoelastic properties of the cellulose fibril/polymer layer.

On a macroscopic level, the interactions between polymers and cellulose fibres were studied by tensile testing. The measurement setup and the materials were chosen so that the specific interactions between the polymers and the fibre surface fibrillation reflected to paper rheology as well as possible. The development of tensile properties upon drying was very characteristic for each polymer and adsorption condition. In addition, the development of drying tension upon drying under uniaxially restricted condition showed differences among the polymers. Hence, this type of research could be useful in optimization of polymer dosing and drying conditions on a paper machine in regard to the desired end properties of a paper product.

Plasticization by moisture clearly influenced the properties of dry paper sheets and the MFC-polymer composite films. CMC increased the plasticization of the composite films, which emphasized the high affinity of the polymer towards moisture. The moisture plasticization of paper sheets in the presence of polymers was different to that of the composite films, suggesting that the polymers have an indirect influence on the moisture plasticization of paper. However, upon consolidation and drying of a paper sheet, the plasticization is considered decisive in regard to the development of fibre bonding and the final properties of dry paper.

The specific behaviour of chitosan as a paper strength additive (in regard to pH of application) was evaluated in more detail in order to gain more insight into the mechanism of action of the polymer and to the interactions between chitosan and cellulose. The adsorption of chitosan on cellulose was influenced by electrostatic interaction but also the presence of a specific non-electrostatic interaction was evident. The pH strongly affected the viscoelastic properties of the chitosan/cellulose layer. In addition, the adhesion between chitosan coated cellulose surfaces was clearly different whether the pH was below or above the solubility limit of the chitosan. The increased adhesion or tackiness of the interface above the solubility limit can be related to the ability of chitosan to improve the strength of a wet paper web. However, the possibility of covalent bonding as a mechanism of action of chitosan was not excluded.

Overall, this thesis work emphasizes the understanding of the interactions between strength enhancing polymers and cellulose fibres from the molecular level onward. When polymeric strength additives are used, it is important to consider not only the basic polymer properties but also the physico-chemical nature of an additive and its interactions with cellulose fibrils and water. In addition, understanding the molecular level interaction between different polymers and cellulose fibrils would be useful in many fields utilizing cellulose.

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